

TANK VAPOR CHARACTERIZATION PROJECT

Headspace Vapor Characterization of Hanford Waste Tank 241-U-112: Results from Samples Collected on 7/9/96

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Summary

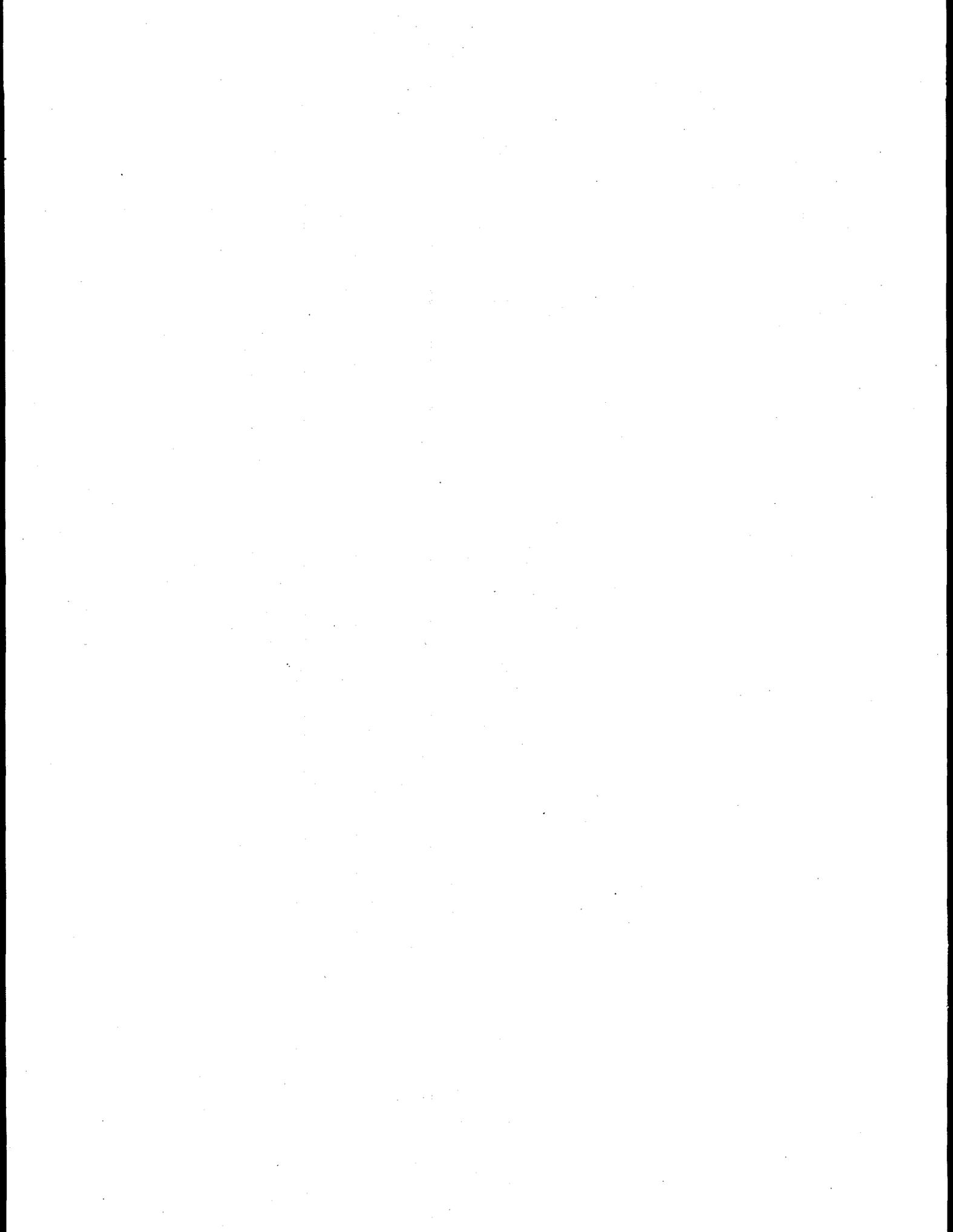
This report describes the analytical results of vapor samples taken from the headspace of the waste storage tank 241-U-112 (Tank U-112) at the Hanford Site in Washington State. The results described in this report were obtained to characterize the vapors present in the tank headspace and to support safety evaluations and tank farm operations. The results include air concentrations of selected inorganic and organic analytes and grouped compounds from samples obtained by Westinghouse Hanford Company (WHC) and provided for analysis to Pacific Northwest National Laboratory (PNNL). Analyses were performed by the Vapor Analytical Laboratory (VAL) at PNNL. Analyte concentrations were based on analytical results and, where appropriate, sample volumes provided by WHC. A summary of the inorganic analytes, permanent gases, and total non-methane organic compounds is listed in Table S.1. The three highest concentration analytes detected in SUMMA™ canister and triple sorbent trap samples are also listed in Table S.1. Detailed descriptions of the analytical results appear in the appendices.

Table S.1. Summary Results of Samples to Characterize the Headspace of Tank U-112 on 7/9/96

<u>Category</u>	<u>Sample Medium</u>	<u>Analyte</u>	<u>Vapor^(a) Concentration</u>	<u>Units</u>
Inorganic Analytes ^(b)	Sorbent Traps	NH ₃	308 ± 15	ppmv
		NO ₂	< 0.16	ppmv
		NO	< 0.16	ppmv
		H ₂ O	13.6 ± 0.6	mg/L
Permanent Gases	SUMMA™ Canister	H ₂	232	ppmv
		CH ₄	< 25	ppmv
		CO ₂	< 17	ppmv
		CO	< 17	ppmv
		N ₂ O	398	ppmv
Total Non-Methane Organic Compounds (TO-12)	SUMMA™ Canister	Non-Methane Organic Compounds	2.03	mg/m ³
Volatile Organics (TO-14)	SUMMA™ Canister	Methanol	1.418	ppmv
		Ethanol	0.494	ppmv
		Propane (TIC)	0.095	ppmv
Semi-Volatile Organics (PNL-TVP-10)	Sorbent Traps	Methanol	0.757	ppmv
		Toluene	0.240	ppmv
		2,4-Dimethylheptane (TIC)	0.234	ppmv

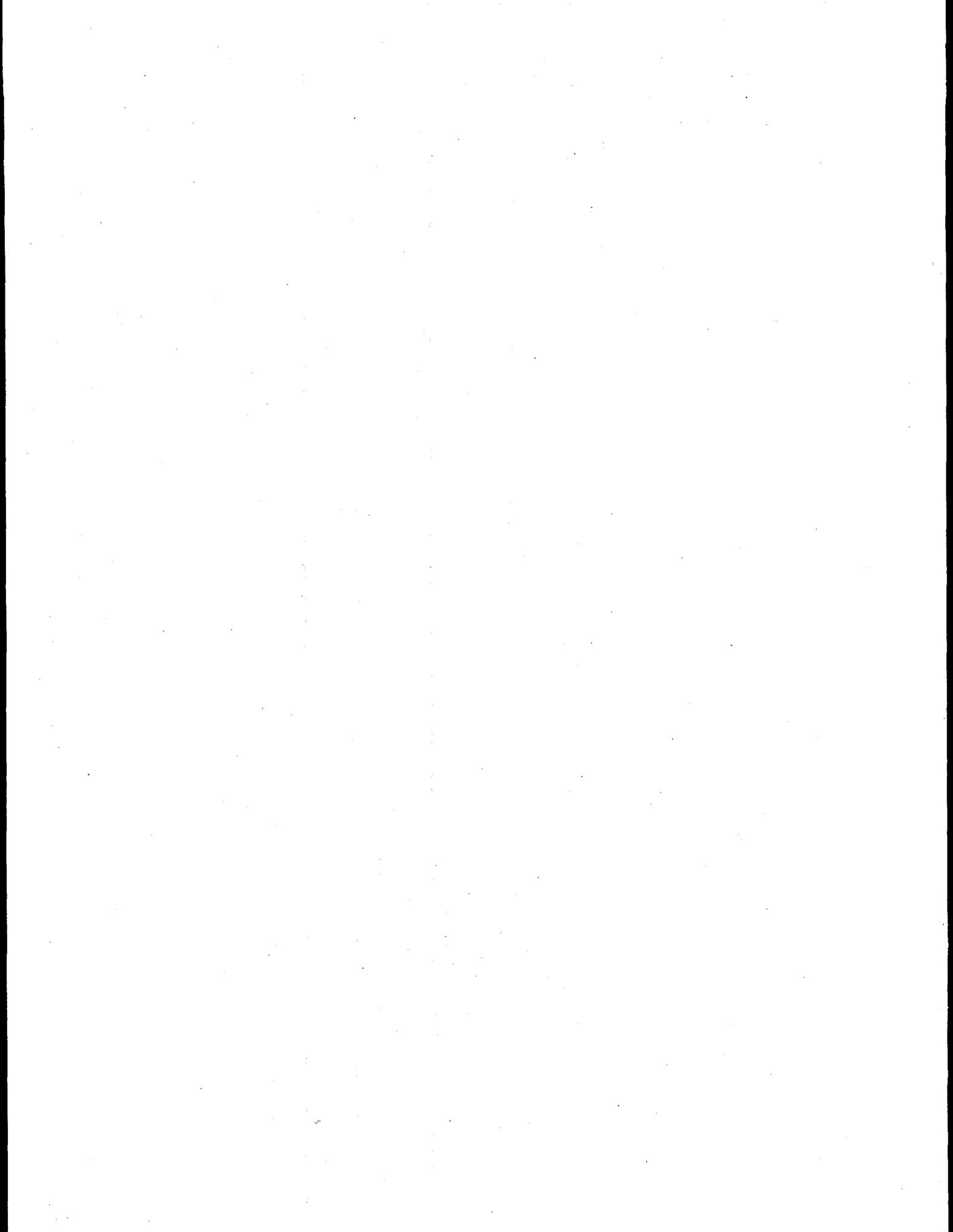
(a) Vapor concentrations were determined using sample-volume data provided by Westinghouse Hanford Company and are based on averaged data.

(b) Inorganic analyte concentrations are based on dry tank air at standard temperature and pressure (STP).



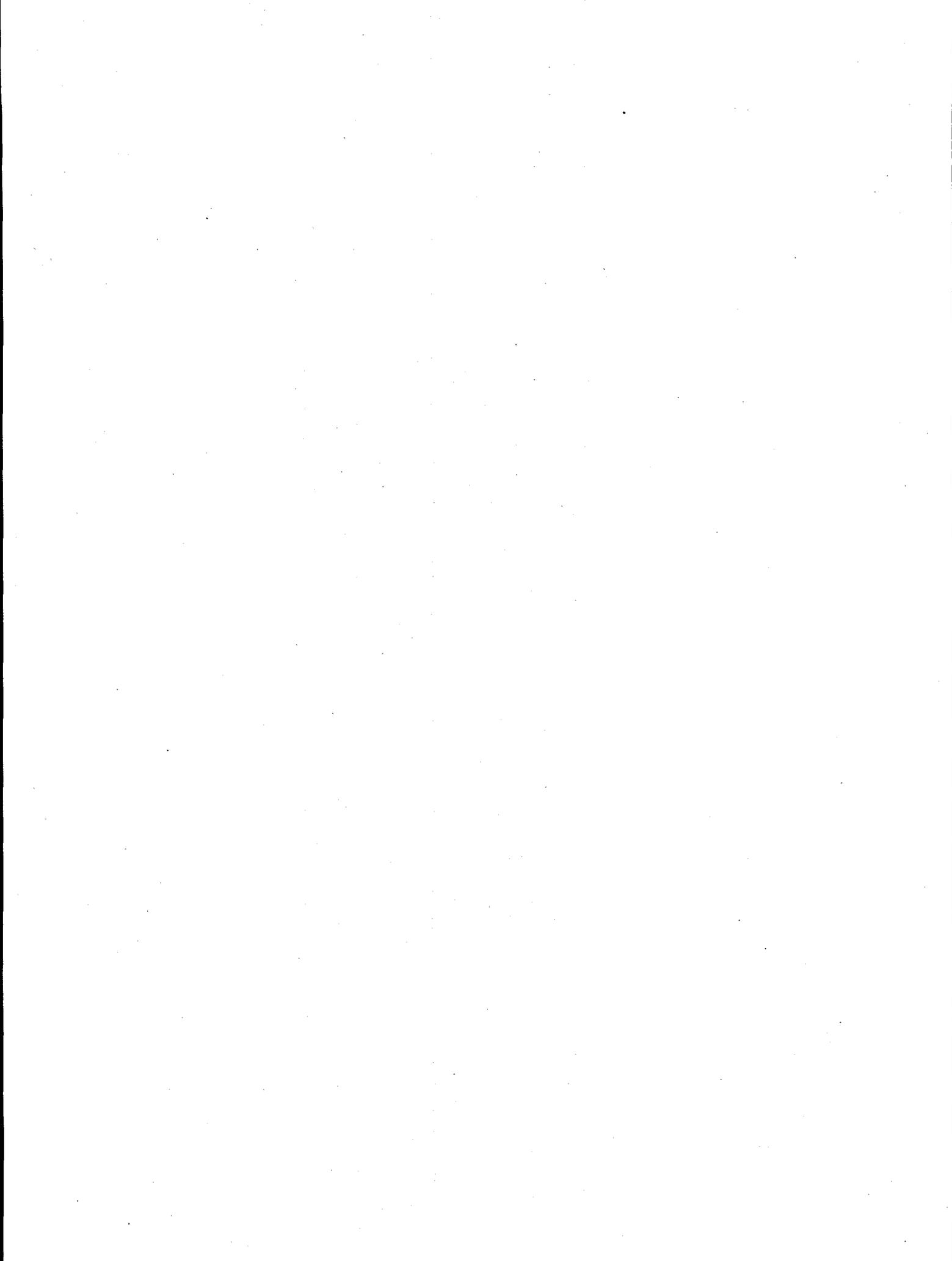
Acknowledgments

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Glossary

% D	% Difference
CAS	Chemical Abstracts Service
CCV	continuing calibration verification
COC	chain-of-custody
C _v	concentration by volume
DIW	deionized water
EPA	U.S. Environmental Protection Agency
GC/FID	gas chromatography/flame ionization detector
GC/MS	gas chromatograph/mass spectrometer
GC/TCD	gas chromatography/thermal conductivity detection
IC	ion chromatography
IL	impact level
IS	internal standard
ISVS	in situ vapor sampling system
MDL	method detection limit
NIST	National Institute for Standards and Technology
PNL	previous designation for Pacific Northwest Laboratory
PNNL	Pacific Northwest National Laboratory
ppbv	part per billion by volume
ppm	parts per million
ppmv	part per million by volume
QA	quality assurance
RPD	relative percent difference
RSD	relative standard deviation
SAP	sample and analysis plan
SCIC	suppressed-conductivity ion chromatography
SRM	standard reference material
STP	standard temperature and pressure
SUMMA™	stainless steel, passivated interior canister
TEA	triethanolamine
TIC	tentatively identified compound
TNMOC	total non-methane organic compounds
TST	triple sorbent trap
UHP	ultra high purity
VAL	Vapor Analytical Laboratory
WHC	Westinghouse Hanford Company



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1.0 Introduction

This report describes the results of vapor samples taken from the headspace of waste storage tank 241-U-112 (Tank U-112) at the Hanford Site in Washington State. Pacific Northwest National Laboratory (PNNL)^(a) contracted with Westinghouse Hanford Company (WHC) to provide sampling devices and analyze samples for inorganic and organic analytes collected from the tank headspace and ambient air near the tank. The analytical work was performed by the PNNL Vapor Analytical Laboratory (VAL) by the Tank Vapor Characterization Project. Work performed was based on a sample and analysis plan (SAP) prepared by WHC. The SAP provided job-specific instructions for samples, analyses, and reporting. The SAP for this sample job was "Vapor Sampling and Analysis Plan" (Homi 1995), and the sample job was designated S6071. Samples were collected by WHC on July 9, 1996 using the In Situ Vapor Sampling System (ISVS).

Sampling devices and controls provided for this job included six sorbent trains for selected inorganic analytes (four sample trains and two field blanks), five SUMMA™ canisters for permanent gases and organic analytes (three samples and two ambient canisters), and eight triple sorbent traps (TSTs) for organic analytes (four samples, two field blanks, and two trip blanks). The samples and controls were provided to WHC on July 8, 1996. Exposed samples and controls were returned to PNNL on July 16, 1996. Samples and controls were handled, stored, and transported using chain-of-custody (COC) forms to ensure sample quality was maintained.

Samples and controls were handled and stored as per PNNL technical procedure PNL-TVP-07^(b), and, upon return to PNNL, were logged into PNNL Laboratory Record Book 55408. Samples were stored at the VAL under conditions (e.g., ambient, refrigerated) required by technical procedures. Access to the samples was controlled and limited to PNNL staff trained in the application of specific technical procedures to handle samples for the tank vapor characterization project. Analyses were performed in the 300 Area at Hanford; specific analytical methods are described in the text. In summary, sorbent traps for inorganic analytes were either weighed (for water analysis) or weighed and desorbed with the appropriate aqueous solutions for analyzing inorganic analytes by either selective electrode or ion chromatography (IC).

Tank headspace samples were analyzed for

- *permanent gases* using gas chromatography/thermal conductivity detection (GC/TCD)
- *total non-methane organic compounds* using cryogenic preconcentration followed by gas chromatography/flame ionization detection (GC/FID)
- *organic analytes* analyses using cryogenic preconcentration followed by gas chromatograph/mass spectrometer (GC/MS)

(a) Pacific Northwest National Laboratory is operated for the U. S. Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. The previous name of the laboratory was Pacific Northwest Laboratory (PNL), which is used when previously published documents are cited.

(b) PNL-TVP-07, Rev. 2, December 1995, *Sample Shipping and Receiving Procedure for PNL Waste Tank Samples*, PNL Technical Procedure, Tank Vapor Project, Pacific Northwest Laboratory, Richland, Washington.

- *organic analytes* (TST samples) using thermal desorption followed by GC/MS.

This report provides summary and detailed analytical information related to the samples and controls. Section 2.0 provides a summary of analytical results. Section 3.0 provides conclusions. Descriptions of samples, analytical methods, quality assurance (QA) and quality control issues, and detailed sample results are provided for each category of samples and analyses in Appendices A, B, C, D, and E. Appendix F contains the completed COC forms.

2.0 Analytical Results

Samples obtained by WHC from the headspace of Tank U-112 on July 9, 1996 (Sample Job S6071) were analyzed in the PNNL Vapor Analytical Laboratory. Summarized results are described in this section; details of samples, analyses, and data tables are provided in the appendices.

2.1 Inorganic Analytes

The vapor concentrations of selected inorganic analytes (NH_3 , NO_2 , and NO) and vapor mass concentration (primarily H_2O) were determined. The average and one standard deviation of concentration results from inorganic sorbent sample trains used to sample headspace vapors were 308 ± 15 ppmv (NH_3), < 0.16 ppmv (NO_2), < 0.16 ppmv (NO), and 13.6 ± 0.6 mg/L (primarily H_2O). The vapor concentration results were based on four samples for each compound. One sample was damaged during disassembly of the sorbent train and was not used in the average for mass gain (see Table A.2). Representative field blanks were also analyzed and used to correct data.

Results provided above are estimated to be accurate to within $\pm 10\%$ (assuming negligible error in the sample volume measurements) and are within the $\pm 30\%$ specified by the SAP. Measurement precision, as indicated by the relative standard deviation, was within 5% for the compounds found to be present at concentrations greater than the analytical method estimated quantitation limit (EQL), and within the 25% specified by the SAP. These uncertainties were confirmed by evaluation of spikes and continuing calibration standards (NH_3 and NO_2) and evaluation of the variability of field blanks (H_2O). All samples were analyzed within 14 days after being collected. No deviations from standard procedures were noted. Data and additional information on samples, analyses, and results are described in Appendix A. The chain-of-custody form used to control samples, 100252, is included in Appendix F.

2.2 Permanent Gases

The complete results of the permanent gas analysis for Tank U-112 can be found in Appendix B. In summary, hydrogen at 232 ppmv and nitrous oxide at 398 ppmv were the only permanent gases detected in the tank headspace samples.

2.3 Total Non-Methane Organic Compounds

The complete results of the TO-12 analysis for Tank U-112 can be found in Appendix C. In summary, the average concentration in the three tank headspace was 2.03 mg/m³. This compares to 6.72 mg/m³ for the sum of all target compounds and tentatively identified compounds (TICs) identified in the analysis of the SUMMA™ canisters.

2.4 Organic Analytes by SUMMA™ Method

The complete results of the SUMMA™ analysis for Tank U-112 can be found in Appendix D. In summary, 56 target analytes above the IDL and four TICs were detected in the tank headspace samples. Fifty-five target analytes and four TICs were identified in two or more tank headspace samples. Methanol at 2.04 mg/m³ and ethanol at 1.02 mg/m³ accounted for 51% of the target compounds and 46% of the total compounds identified in the analysis. The total concentration of the target analytes was 5.98 mg/m³. Propane (0.19 mg/m³) and hexamethylcyclotrisiloxane (0.04 mg/m³) were the two highest concentration TICs found in two or more of the tank headspace samples. The total concentration of TICs identified was 0.74 mg/m³. The total concentration of all the compounds identified was 6.72 mg/m³. This compares to a total concentration of 2.03 mg/m³ identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 183 was analyzed in replicate for target analytes and TICs to determine analytical precision. Forty-nine of 55 target compounds and three of four TICs had relative percent differences (RPDs) of less than 10%.

Fifty-five target compounds and one TIC were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels. Trace levels of many of the target analytes may be false positives due to the fact that some of the compounds were found in the continuing calibration blank (CCB) above the EQL and are greater than 20 times the concentration found in the sample. These compounds are flagged with a "B" in the tables.

2.5 Organic Analytes by Triple Sorbent Trap Method

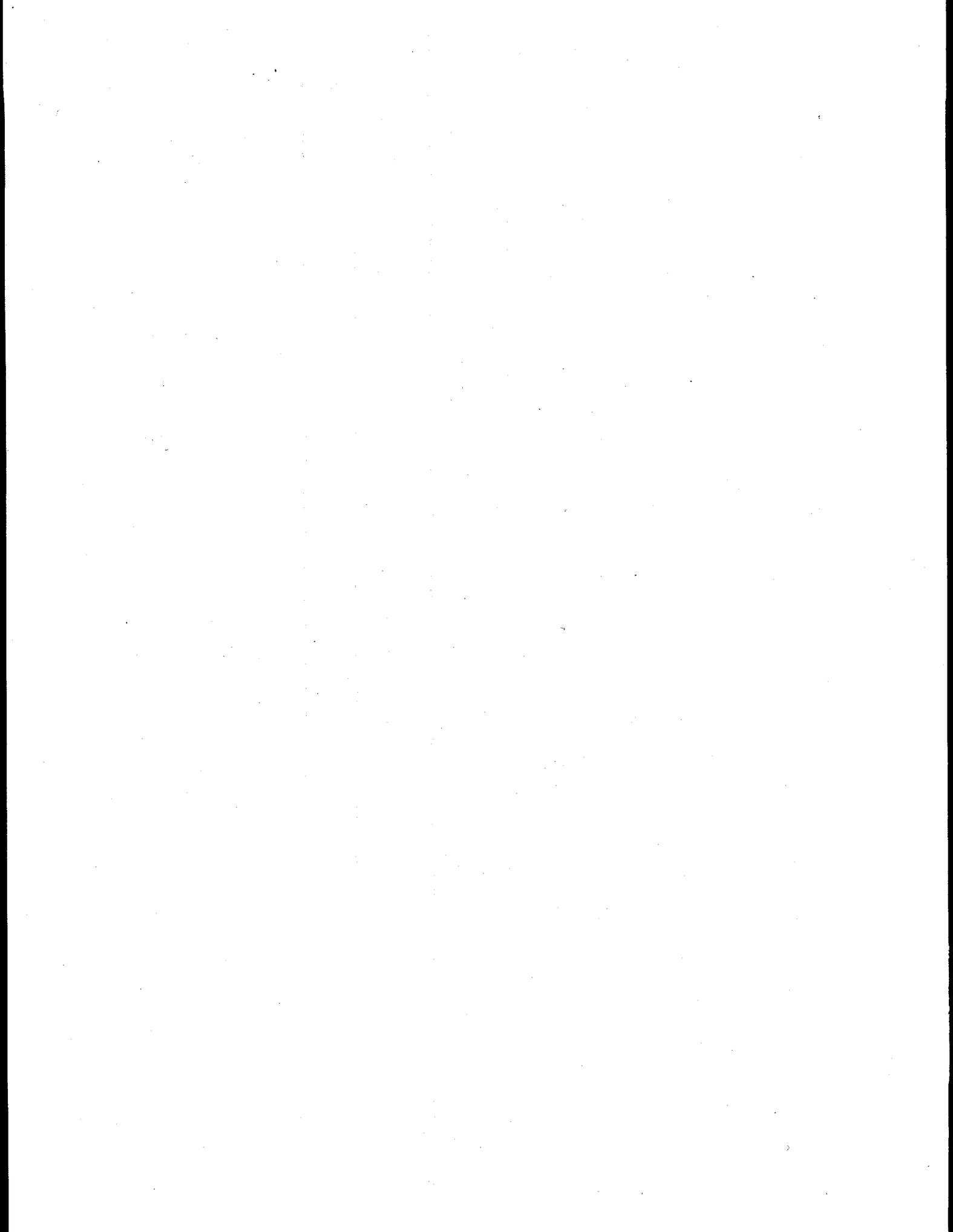
The complete results of the sorbent trap analysis for Tank U-112 can be found in Appendix E. In summary, 44 target analytes above the IDL and 20 TICs were detected in the tank headspace samples. All 44 of the target analytes and 20 TICs were observed in two or more sorbent traps. Methanol at 1.08 mg/m³ and toluene at 0.99 mg/m³ accounted for 38% of the target analytes and 15% of the total concentration identified by the analysis. The total concentration of the target analytes was 5.42 mg/m³ or 39% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 2,4-dimethylheptane at 1.34 mg/m³ and hexamethylcyclotrisiloxane at 1.12 mg/m³. The total concentration of the TICs was 8.56 mg/m³ or 61% of the total concentration identified by analysis. The total concentration of all the compounds identified was 13.98 mg/m³.

Triple sorbent trap sample PNL 1091 was analyzed in replicate for target analytes and TICs to determine analytical precision. Thirty-one of 43 target compounds and 17 of 19 TICs had RPDs of less than 10%.

The field blanks are badly contaminated with a group of compounds characteristic of the 3M adhesive tape used on previous ISVS jobs. Because of the tape problem and other environmental blanks problems incurred during sampling, tank results from this sampling activity should generally be considered as suspect.

3.0 Conclusions

The concentrations of inorganic and organic analytes were determined from samples of the headspace of Tank U-112 on July 9, 1996 (Sample Job S6071). The vapor concentrations were based either on whole-volume samples (SUMMA™ canisters) or on sorbent traps exposed to sample flow. In the case of the canisters, the concentrations were based on analytical results and the tracking of dilution/concentration of sample volumes obtained directly from the canisters. In the case of the sorbent traps, concentrations were based on analytical results and sample volumes reported by WHC. Known sampling and analytical variances from established quality assurance requirements, where significant, were documented in this report, as required by the SAP (Homi 1995). WHC was immediately notified based on preliminary, uncorrected analytical results, when the ammonia concentration was determined to be above the notification level of 150 ppmv. Notification levels and notification procedures are described in the SAP (Homi 1995).



4.0 Reference and Further Reading

Reference

Homi, C.S. 1995. *Vapor Sampling and Analysis Plan*. WHC-SD-WM-TP-335, Rev. 2A, Westinghouse Hanford Company, Richland, Washington.

Further Reading

Pacific Northwest Laboratory. *Analytical Laboratory Procedure Compendium*. Procedure PNL-ALO-271. PNL-MA-599, Pacific Northwest Laboratory, Richland, Washington.

Pacific Northwest Laboratory. *Quality Assurance Manual, Part 3: Procedures for Quality Assurance Program*. PNL-MA-70, Part 3, Pacific Northwest Laboratory, Richland, Washington.

Pacific Northwest National Laboratory. *Quality Assurance Plan for Activities Conducted by the Pacific Northwest National Laboratory Vapor Analytical Laboratory (VAL) and the Pacific Northwest National Laboratory Tank Vapor Characterization Project*. ETD-002, Rev. 0, Pacific Northwest National Laboratory, Richland, Washington.

U.S. Department of Energy. *Hanford Analytical Services Quality Assurance Plan (HASQAP)*. DOE/RL-94-55, Rev. 2, U. S. Department of Energy, Richland, Washington.

Westinghouse Hanford Company. *Quality Assurance Project Plan for Tank Vapor Characterization*. WHC-SD-WM-QAPP-013, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Appendix A

Tank Vapor Characterization:

Inorganic Analytes

Appendix A

Tank Vapor Characterization: Inorganic Analytes

Solid sorbent traps, prepared in multi-trap sampling trains, were supplied to Westinghouse Hanford Company (WHC) for sampling the tank headspace using the In Situ Vapor Sampling System (ISVS). Blanks, spiked blanks (when requested), and exposed samples were returned to Pacific Northwest National Laboratory (PNNL) for analysis. Analyses were performed to provide information on the tank headspace concentration of the following analytes: ammonia (NH_3), nitrogen dioxide (NO_2), nitric oxide (NO), and water (H_2O). Procedures were similar to those developed previously during sample jobs performed with the VSS connected to the headspace of Tank C-103 (Ligotke et al. 1994). During those sample jobs, control samples provided validation that the sorbent tubes effectively trapped NH_3 and mass. Samples were prepared, handled, and disassembled as described in Technical Procedure PNL-TVP-09^(a). Analytical accuracy was estimated based on procedures used. Sample preparation and analyses were performed following PNNL quality assurance (QA) impact level II requirements.

A.1 Sampling Methodology

Standard glass tubes containing sorbent materials to trap vapors of selected analytes of NH_3 , NO, NO_2 , and H_2O (supplied by SKC Inc., Eighty Four, Pennsylvania) were obtained, prepared, and submitted for vapor sampling. The sorbent traps were selected based on their use by the Occupational Safety and Health Administration to perform workplace monitoring and because of available procedures and verification results associated with that particular application. The typical sorbent traps used consisted of a glass tube containing a sorbent material specific to the compound of interest. In general, the tubes contained two sorbent layers, or sections; the first layer was the primary trap, and the second layer provided an indication of breakthrough. In the tubes, sorbent layers are generally held in packed layers separated by glass wool. The sorbent traps, with glass-sealed ends, were received from the vendor.

The type and nominal quantity of sorbent material varied by application. Sorbent traps were selected for the tank sample job and included the following products. The NH_3 sorbent traps contained carbon beads impregnated with sulfuric acid; nominally, 500 mg were contained in the primary and 250 mg in the breakthrough sections. The NH_3 was chemisorbed as ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$]. The NO_2 traps contained a zeolite impregnated with triethanolamine (TEA), with 400 mg in the primary and 200 mg in the breakthrough sections. The NO_2 was absorbed and disproportionated to equi-molar quantities of nitrite ions (NO_2^-) and nitrate ions (NO_3^-). Glass tubes containing 800 mg of an oxidant such as chromate were used to convert NO to NO_2 . The converted NO was then collected as nitrite and nitrate in an NO_2 trap. The water traps contained 300 mg of silica gel in the primary and 150 mg in the breakthrough sections.

^(a) Pacific Northwest Laboratory. 12/95. *Sorbent Trap Preparation for Sampling and Analysis: Waste Tank Inorganic Vapor Samples*, PNL-TVP-09 (Rev. 2), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Sorbent trains provided to trap inorganic compounds included all or some of the following: samples, spiked samples, spares, blanks, and spiked blanks. Sorbent trains were prepared from same-lot batches, with the oxidizer sections of the NO_x sorbent trains having been stored previously in a freezer. After sample preparation, sorbent trains were stored at ≤ 10°C because of handling recommendations for the oxidizer tubes attached to some samples. After receipt of exposed and radiologically cleared samples from WHC and disassembly of the sorbent trains, samples were provided to the analytical laboratory at ambient temperature.

The sorbent traps were prepared in multi-trap sorbent trains configured so sample flow passed in order through the traps, targeting specific analytes, and then through a desiccant trap. The specific order of traps within the various sorbent trains is described in Section A.4. The ends of the glass-tube traps were broken, and the traps were weighed and then connected to each other using uniform lengths of 3/8-in. perfluoroalkoxy-grade Teflon® tubing. The tubing was heated in hot air and forced over the open ends of the traps to form a tight seal. The inlets of the sorbent trains each consist of a short section of tubing that has a 3/8-in. stainless steel Swagelok® nut, sealed using a Swagelok® cap. The trailing ends of the sorbent trains (the downstream end of the traps containing silica gel) were each sealed with red plastic end caps provided by the manufacturer. The sorbent-tube trains remained sealed other than during the actual sampling periods. During vapor sampling, C-Flex® tubing was provided by WHC to connect the downstream ends of the sorbent trains to the sampling manifold exhaust connections.

A.1.1 Concentration Calculations. The concentrations of target compounds in the tank headspace were determined from sample results, assuming effective sample transport to the sorbent traps. Concentration, in parts per million by volume (ppmv), was determined by dividing the mass of the compound, in μmol, by the volume of the dried tank air sampled in moles. The micromolar sample mass was determined by dividing the compound mass, in μg, by the molecular weight of the compound, in g/mol. The molar sample volume was determined, excluding water vapor, by dividing the standard sample volume (at 0°C and 760 torr), in L, by 22.4 L/mol. For example, the concentration by volume (C_v) of a 3.00-L sample containing 75.0 μg of NH₃ equals

$$C_v = \frac{75.0 \mu\text{g}}{17.0 \text{ g/mol}} \left[\frac{3.00 \text{ L}}{22.4 \text{ L/mol}} \right]^{-1} = 32.9 \text{ ppmv} \quad (\text{A.1})$$

This calculational method produces concentration results that are slightly conservative (greater than actual) because the volume of water vapor in the sample stream is neglected. The volume of water vapor is not included in the measured sampled volume because of its removal in desiccant traps upstream of the mass flowmeter. However, the bias is generally expected to be small. For a tank headspace temperature of 35°C, the magnitude of the bias would be about 1 to 6%, assuming tank headspace relative humidities of 20 to 100%, respectively. The concentration of mass (determined gravimetrically) was also per dry-gas volume at standard conditions.

A.2 Analytical Procedures

The compounds of interest were trapped using solid sorbents and chemisorption (adsorption of water vapor). Analytical results were based on extraction and analysis of selected ions. Analytical procedures used are specified in the text.

A.2.1 Ammonia Analysis. The sorbent material from the NH_3 -selective sorbent traps was placed into labeled 20-mL glass scintillation vials. Vials containing front-, or primary-, section sorbent material were treated with 10.0 mL of deionized water (DIW), and vials containing back-up-section sorbent material were treated with 5.0 mL of DIW. After extraction, the NH_3 sorbent traps were analyzed using the selective ion electrode procedure PNL-ALO-226 Rev. 0^(a). Briefly, this method includes 1) preparing a 1000- $\mu\text{g}/\text{mL}$ (ppm) NH_3 stock standard solution from dried reagent-grade NH_4Cl and DIW, 2) preparing 0.1-, 0.5-, 1.0-, 10-, and 100-ppm NH_3 working calibration standards by serial dilution of the freshly made stock standard, 3) generating an initial calibration curve from the measured electromotive force signal versus NH_3 concentration data obtained for the set of working standards, 4) performing a calibration-verification check, using a mid-range dilution of a certified National Institute for Standards and Technology (NIST)-traceable 0.1 M NH_4Cl standard from an independent source, after analyzing every five or six samples, 5) continuing this sequence until all samples of the batch have been measured, including duplicates and spiked samples, and 6) remeasuring the complete set of calibration standards (at the end of the session). Electromotive force (volts) signal measurements obtained for samples are compared to those for standards, either graphically or algebraically (using linear regression) to determine NH_3 concentration in the samples.

A.2.2 Nitrite Analysis. The sorbent traps for NO_2 and NO were desorbed in an aqueous TEA and n-butanol solution and analyzed by suppressed-conductivity ion chromatography (SCIC) for nitrite according to PNL-ALO-212, Rev. 1^(b) modified to obviate interferences by concentrations of non-target analytes. Specifically, the modifications used were 1) eluent 1.44 mM Na_2CO_3 + 1.8 mM NaHCO_3 at 2.0 mL/min, 2) one guard column (AG4A) and two separator columns (AS4A) in series instead of just one separator column, and 3) all standards, samples, and blanks were injected into the IC sample loop through 0.45- μm syringe filters.

For the analysis, the sorbent materials were placed into labeled 20-mL glass scintillation vials. To each vial, 3.0 mL of desorbing solution (15 g TEA + 1 mL n-butanol in 1.0 L of DIW) was added. Primary sorbent-tube sample materials and back-up (breakthrough) sorbent-trap materials were analyzed separately using identical procedures. Each analytical session was conducted as follows. Working nitrite standards (0, 0.1, 0.25, and 0.5 ppm) were prepared by diluting a stock nitrite standard with desorbing solution. An initial calibration curve was prepared from the instrument response (chromatographic peak height) versus nitrite standard concentration data for the set of working standards. A calibration verification check using one of the midrange standards was

(a) Procedure entitled "Ammonia (Nitrogen) in Aqueous Samples," PNL-ALO-226, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.

(b) Procedure entitled "Determination of Inorganic Anions by Ion Chromatography," PNL-ALO-212, in the *Analytical Chemistry Laboratory (ACL) Procedure Compendium*, Vol. 3: Inorganic Instrumental Methods. Pacific Northwest Laboratory, Richland, Washington.

performed after the analysis of every six samples. If the instrument response indicated that sample nitrite concentration was outside the calibration range (> 0.5 ppm nitrite), the sample was diluted with desorbing solution and reanalyzed. After all samples of a batch were analyzed, the complete set of calibration standards was remeasured to verify consistent instrument response, and the analytical session was terminated.

Instrument responses (peak height) observed for samples were compared to those for standards to determine the nitrite concentration of the samples. Because NO_2 and NO converted to NO_2 were collected on the sorbent as equal quantities of nitrite and nitrate, and the analysis was specific for nitrite, the molar masses of NO_2 and NO were determined by doubling the analytically determined molar mass of nitrite.

A.2.3 Mass (Water) Analysis. Sorbent traps used to make each sample train were weighed using a semi-micro mass balance, after labeling and breaking the glass tube ends, without plastic end caps in accordance with procedure PNL-TVP-09. After receipt of exposed samples, the sorbent traps were again weighed to determine the change in mass. Records of the measurements were documented on sample-preparation data sheets. The mass concentration, generally roughly equal to the concentration of water, was determined by dividing the combined change in mass from all traps in a sorbent train by the actual volume of gas sampled. Field blanks were used to correct results.

A.3 Quality Assurance/Quality Control

Analytical work was performed according to quality levels identified in the project QA plan and several PNNL documents including PNL-MA-70 (Part 3), PNL-ALO-212, PNL-ALO-226, and Quality Assurance Plan ETD-002. The samples were analyzed following PNNL Impact Level II. A summary of the analysis procedures and limits for the target inorganic compounds is provided in Table A.1. The table also shows generic expected notification ranges and describes related target analytical precision and accuracy levels for each analyte; the information in the table is based on the data quality objective assessment by Osborne et al. (1995). From the table, it can be seen that the EQL required to resolve the analyte at one-tenth of the recommended exposure limit for each of the target analytes is achieved using current procedures and with a vapor-sample volume of 3 L and a desorption-solution volume of 3 mL (10 mL for NH_3).

The accuracy of concentration measurements depends on potential errors associated with both sampling and analysis (see Section A.4). Sampling information, including sample volumes, was provided by WHC; sample-volume uncertainty was not provided. The uncertainty of analytical results, which depends on the method used, was estimated to be within allowable tolerances (Osborne et al. 1995; Table A.1). For NH_3 analyses, the accuracy of laboratory measurements by selective ion electrode was estimated to be $\pm 5\%$ relative, independent of concentration at $1 \mu\text{g}/\text{mL}$ or greater levels. The uncertainty includes preparation of standards, purity of the ammonium salt used to prepare standards, potential operator bias, ambient temperature variations, etc. Working standards are traceable to NIST standard reference material (SRM) by using an independent calibration verification standard certified to be NIST traceable. Nitrite analyses (for NO_2 and NO) are performed using certified but not NIST-traceable SRM; this is because NIST does not make a nitrite SRM. Based on experience in comparing nitrite working standards prepared from several different sources and factors mentioned for NH_3 above, the estimated maximum bias for samples derived from sampling for NO_2 is $\pm 10\%$, and for samples derived from sampling for NO it is $\pm 5\%$ relative.

Table A.1. Analytical Procedures, Quantification Limits, and Notification Levels for Selected Inorganic Analytes^(a)

Analyte	Formula	Procedure	EQL ^(b) (μg)	EQL ^(b) (ppmv)	Notification Level ^(c) (ppmv)
Ammonia	NH ₃	PNL-ALO-226	1.0	0.71	≥ 150
Nitrogen Dioxide	NO ₂	PNL-ALO-212	0.3	0.16	≥ 10
Nitric oxide	NO	PNL-ALO-212	0.3	0.16	≥ 50
Mass (water) ^(d)	n/a	PNL-TVP-09	0.6 mg	0.3 mg/L	n/a

(a) Analytical precision and accuracy targets for results in the expected ranges equal $\pm 25\%$ and 70 to 130%, respectively (Osborne et al. 1995).

(b) The lowest calibration standard is defined as the EQL.

(c) As per Table 7-1 in Osborne et al. (1995). Notification levels require verbal and written reports to WHC on completion of preliminary analyses.

(d) The vapor-mass concentration, thought to be largely water vapor, is determined gravimetrically.

n/a = not applicable.

The accuracy of measurements of sample mass is typically ± 0.1 mg, or much less than 1% of the mass changes of most samples. The analytical accuracy of measurements of the change in mass of sorbent trains, based on the variability in mass change of field-blank sorbent trains, is determined for each sample job and is typically about ± 1 mg per five-trap sorbent train.

A.4 Inorganic Sample Results

Samples were obtained by WHC from the tank headspace of Tank U-112 on July 9, 1996 using the ISVS. The sample job designation number was S6071. Samples were prepared, submitted to WHC for the sample job, and then returned to PNNL and analyzed to provide information on the concentrations of NH₃, NO₂, NO, and mass (primarily H₂O). Samples were controlled using COC form 100252 (Appendix F). The inorganic samples and sample volume information were received from WHC on July 16, 1996. Analyses were completed on July 18, 1996 (gravimetric, 9 days elapsed), July 23, 1996 (ammonia, 14 days elapsed), and July 22, 1996 (nitrite, 13 days elapsed).

A list of samples, sampling information, sample volumes, and gravimetric results is shown in Table A.2. The types of sample trains used and the order of sorbent traps within each train are also shown in the table. For example, the sorbent train NH₃/NO_x/H₂O contained an NH₃ trap at the inlet end, a NO_x series in the middle (Section A.4.2), and a desiccant trap at the outlet end. Analytical mass and concentration results are shown in Table A.3. Sample volumes were provided by WHC; sample-volume uncertainty was not provided. Tank headspace concentration results (Table A.3) are based on this information, and the listed uncertainties equal plus or minus one standard deviation of the individual results from each set of samples. Percentage relative standard deviation (RSD) may be determined by dividing the standard deviation by the average result and multiplying by 100. Where analytical results from samples, corrected for blanks, were less than the EQL in Table A.1, the concentration results (Table A.3) are listed as "less-than" the EQL value. Results of control samples,

such as trip blanks, field blanks, and spiked blanks, are discussed in this section. Spiked blanks, when used, were transported to the field but not opened. Spiked samples, when used, were opened in the field and used to collect tank vapors. Sample results were not corrected for the percentage recoveries of spiked blanks.

A.4.1 Ammonia Results. The concentration of NH_3 was 308 ± 15 ppmv, based on all four samples. The blank-corrected NH_3 quantities in the sorbent traps ranged from 24.0 to 27.1 μmol in front sections; blank-corrected NH_3 was not found ($\leq 0.01 \mu\text{mol}$) in back sorbent sections. Blank corrections, 0.43 μmol in front and 0.06 μmol in back sections, were about 2% of collected quantities. The analysis of one sample was duplicated and yielded a repeatability of $\pm 3.2\%$. One blank sorbent trap was spiked with 17 μmol of NH_3 and yielded a percentage recovery of 109%. One sample leachate was spiked after initial analysis with roughly the quantity of ammonia in the sample and yielded a percentage recovery of 95%. The initial and continuing calibration verification standards, using NIST-traceable material, yielded percentage recoveries of 97% (ICV) and 103, 97, 101, 104, and 104% (CCV) during the analytical session. A 5-point calibration was performed over an NH_3 range of 0.1 to 1000 $\mu\text{g/mL}$.

A.4.2 Nitrogen Oxides Results. The concentrations of NO_2 and NO were both < 0.16 ppmv based on all four samples. Blank-corrected NO_2^- quantities in the sorbent traps were all $< 0.013 \mu\text{mol}$. Nitrite blank levels used to correct data were 0.0062 μmol in front (four of four blanks analyzed) and 0.0036 μmol in back (two of four blanks analyzed) sorbent sections. The analyses of two samples were duplicated and yielded repeatabilities of $\pm 2.0\%$ and $\pm 6.8\%$. Two sample leachates were spiked with 0.125 ppm NO_2^- and yielded percentage recoveries of 97 and 92%. A 4-point calibration was performed over a concentration range of 0 to 0.5 $\mu\text{g NO}_2^-$ per mL in the desorbing matrix. Although spiked blanks were not tested, blanks spiked with 0.0064, 0.047, 0.11, and 0.74 $\mu\text{mol NO}_2^-$ during previous sample jobs yielded percentage recoveries of 153 ± 14 , 103 ± 4 , 106 ± 8 , and $111 \pm 7\%$, respectively (Clauss et al. 1994; Ligothke et al. 1994).

A.4.3 Gravimetric Results. Gravimetric results yield water vapor concentrations. This is because the total mass concentration of other vapors in the headspaces of Hanford waste tanks, measured in $\mu\text{g/L}$, are typically two or three orders of magnitude less than the mg/L mass concentrations of the water vapor found in even relatively dry tanks. The water vapor mass concentration collected in the 5-trap sorbent trains was $13.6 \pm 0.6 \text{ mg/L}$, based on dry air sample volumes (0°C and 760 torr). The result was determined from an average mass gain of 28.9 mg from three of four sample trains. The blank correction applied to the results was - 3.6 mg per train, based on a mass gain of $3.6 \pm 0.0 \text{ mg}$ per two 5-trap field-blank sorbent trains. A control mass was measured and indicated a measurement accuracy of $\pm 0.1 \text{ mg}$. Although no spiked blanks were tested, the percentage recovery of mass from three blank H_2O traps spiked with 51 mg water was $103 \pm 2\%$ during a previous sample job (Clauss et al. 1994).

Corrected for a measured tank headspace temperature of 18.3°C and pressure of 738.6 torr, the actual water vapor mass concentration from the gravimetric results was $12.2 \pm 0.6 \text{ mg/L}$. Also based on analytical results, the partial pressure of water vapor was $12.3 \pm 0.6 \text{ torr}$, the relative humidity was $78 \pm 4\%$, and the dew point was $14.4 \pm 0.7^\circ\text{C}$.

Table A.2 List of PNNL Inorganic Samples, Controls, and Gravimetric Results
Obtained from the Headspace of Tank U-112 on 7/9/96

Sample Number	Sorbent Train Type	Sample Port and Volume Information ^(a)				
		Sample Port	Flow Rate (mL/min)	Duration (min)	Volume (L)	Mass Gain (g)
<u>Samples:</u>						
S6071-A07-28R	NH3/NOx/H2O	1	200.0	10.0	1.86	0.0175 x
S6071-A08-29R	NH3/NOx/H2O	2	200.0	10.0	1.86	0.0276
S6071-A09-30R	NH3/NOx/H2O	3	200.0	10.0	1.86	0.0293
S6071-A10-31R	NH3/H2O/H2O	4	200.0	10.0	1.86	0.0299
<u>Controls:</u>						
S6071-A15-32R	NH3/NOx/H2O Field Blank	n/a ^(b)	n/a	n/a	n/a	0.0036
S6071-A16-33R	NH3/NOx/H2O Field Blank	n/a	n/a	n/a	n/a	0.0036

(a) Sampling information and dry-gas sample volumes, corrected to 0°C and 760 torr, were provided by WHC. Uncertainty values were not provided with sample-volume results.

(b) n/a = not applicable.

x Lost glass chip during disassembly of sample sorbent train.

Table A.3 Inorganic Vapor Sample Results Obtained from the Headspace of Tank U-112 on 7/9/96

Sample	Analytical Results (μmol)			Sample Volume (L)	Vapor ^(a) Concentration (ppmv)
	Front Section	Back Section	Total ^(b) Blank-Corrected		
<u>NH₃ Samples:</u>			<u>25.5</u>	<u>1.86</u>	<u>308 ± 15</u>
S6071-A07-28R	26.2	0.052	25.8	1.86	310
S6071-A08-29R	24.4	NA ^(c)	24.0	1.86	289
S6071-A09-30R	25.8	0.073	25.4	1.86	306
S6071-A10-31R	27.5	NA	27.1	1.86	326
<u>NO₂ Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6071-A07-28R	0.0065	NA	<0.013	1.86	<0.16
S6071-A08-29R	0.0069	0.0028	<0.013	1.86	<0.16
S6071-A09-30R	0.0058	NA	<0.013	1.86	<0.16
S6071-A10-31R	0.0059	0.0031	<0.013	1.86	<0.16
<u>NO Samples:</u>			<u><0.013</u>	<u>1.86</u>	<u><0.16</u>
S6071-A07-28R	0.0073	0.0051	<0.013	1.86	<0.16
S6071-A08-29R	0.0065	NA	<0.013	1.86	<0.16
S6071-A09-30R	0.0070	0.0034	<0.013	1.86	<0.16
S6071-A10-31R	0.0074	NA	<0.013	1.86	<0.16
<u>Gravimetric Samples:</u>			<u>25.3 mg</u>	<u>1.86</u>	<u>13.6 ± 0.6 mg/L</u>
S6071-A07-28R	n/a ^(c)	n/a	13.9 x ^(c)	1.86	7.5 x
S6071-A08-29R	n/a	n/a	24.0	1.86	12.9
S6071-A09-30R	n/a	n/a	25.7	1.86	13.8
S6071-A10-31R	n/a	n/a	26.3	1.86	14.1

- (a) Blank-corrected vapor concentrations were calculated using WHC-reported dry-air sample volumes (Table A.2). In the calculation for concentration, the nitrite values (listed) were doubled to account for unanalyzed nitrite. Sample results were not corrected for percentage recovery of spiked samples or spiked blanks. Underlined values represent the average of the set of samples. Concentration uncertainty equals ± 1 standard deviation (absolute) for each set of samples. Percentage RSD may be determined by dividing standard deviation by the average and multiplying the result by 100. The use of "<" is defined in Section A.4.
- (b) Total blank-corrected analyte masses (nitrite for NO₂ and NO) were determined, when significant, by subtracting the quantity of analyte found in blanks from that found in samples. The level of analytes found in blanks is described in the subsections of Section A.4.
- (c) NA = not analyzed; n/a = not applicable; x = excluded from average.

A.5 References

Clauss, T. W., M. W. Ligothke, B. D. McVeety, K. H. Pool, R. B. Lucke, J. S. Fruchter, and S. C. Goheen. 1994. *Vapor Space Characterization of Waste Tank 241-BY-104: Results from Samples Collected on 6/24/94*. PNL-10208. Pacific Northwest National Laboratory, Richland, Washington.

Ligothke, M. W., K. H. Pool, and B. D. Lerner. 1994. *Vapor Space Characterization of Waste Tank 241-C-103: Inorganic Results from Sample Job 7B (5/12/94 - 5/25/94)*. PNL-10172, Pacific Northwest National Laboratory, Richland, Washington.

Osborne, J. W., J. L. Huckaby, E. R. Hewitt, C. M. Anderson, D. D. Mahlum, B. A. Pulsipher, and J. Y. Young. 1995. *Data Quality Objectives for Generic In-Tank Health and Safety Vapor Resolution*. WHC-SD-WM-DQO-002, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Appendix B

Tank Vapor Characterization:

Permanent Gases

Appendix B

Tank Vapor Characterization: Permanent Gases

B.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. If the canister is verified as clean by TO-12, the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

B.2 Analytical Procedure

The SUMMA™ canister samples were analyzed for permanent gases according to PNNL Technical Procedure PNL-TVP-05^(b) with the exceptions listed in the following text and in the quality assurance/quality control section of this report. This method was developed in-house to analyze permanent gases, defined as hydrogen (H₂), carbon dioxide (CO₂), carbon monoxide (CO), methane (CH₄), and nitrous oxide (N₂O), by gas chromatograph/thermal conductivity detection (GC/TCD). Aliquots of sampled air are drawn directly from each canister into a 5-mL gas-tight syringe and injected into a Hewlett-Packard 5890 GC/TCD fitted with a loop injector valve and a column switching valve. An aliquot of 5 mL is used so that the 1.0-mL injection loop is completely purged with sample air, ensuring that no dilution of the sample takes place within the injection loop. One set of GC conditions is used to analyze for CO, CO₂, N₂O, and CH₄ using Helium (He) as the carrier gas. A second GC analysis is performed for H₂ (using nitrogen as the carrier gas) to enhance the signal sensitivity and lower the detection limit for this analyte. The permanent gases and associated EQLs are listed in Table B.1.

^(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

^(b) Pacific Northwest Laboratory. 5/96. *Analysis Method for the Determination of Permanent Gases in Hanford Waste Tank Vapor Samples Collected in SUMMA™ Passivated Stainless Steel Canisters*, PNL-TVP-05 (Rev. 2). PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Table B.1. Analytical Procedures and Detection Limits for Permanent Gases

<u>Analyte</u>	<u>Formula</u>	<u>Procedure</u>	<u>Estimated Quantitation Limit (ppmv)</u>
Carbon Dioxide	CO ₂	PNL-TVP-05	17
Carbon Monoxide	CO	PNL-TVP-05	17
Methane	CH ₄	PNL-TVP-05	25
Hydrogen	H ₂	PNL-TVP-05	17
Nitrous Oxide	N ₂ O	PNL-TVP-05	17

B.3 Quality Assurance/Quality Control

Standards for the permanent gas analysis were blended from commercially prepared and certified standards for each of the analytes reported in Table B.1. The instrument was calibrated for CH₄ over a range of 25 to 2100 parts per million by volume (ppmv) and for CO, CO₂, and N₂O over a range of 17 to 2100 ppmv using standards at five different concentrations and He as a carrier gas. A similar procedure was followed for H₂ with a range of 17 to 2120 ppmv, except the carrier gas was changed to N₂. An average response factor from the calculation was used for quantification of compound peak area.

Each analyte was quantitated by comparison of sample analyte peak area to the calibration plot generated for the compound. The estimated quantitation limit (EQL) for the method has been established as the low level calibration standard. Before and after each sample analysis set, a gas standard was run to evaluate system performance and to measure system accuracy. The calculated concentration of the individual gases in the standards fell within $\pm 25\%$ of the expected concentrations. One sample was run in duplicate to provide a measure of method precision. Results of the replicate analysis are presented in Table B.2. An N₂ reagent blank, an ambient-air sample collected ~10 m upwind of Tank U-112 and the ambient air collected through the In Situ Vapor Sampling System (ISVS) were used as method blanks and used to determine the potential for analyte interferences in the samples.

B.4 Permanent Gases Sample Results

Table B.2 lists results of the permanent gas analysis from samples collected from the headspace of Tank U-112, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on August 21 and 22, 1996. Hydrogen at an average concentration of 232 ppmv and nitrous oxide at an average concentration of 398 ppmv were the only permanent gases observed above the EQL in the tank headspace samples. A replicate analysis was performed on SUMMA™ canister PNL 183; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

Table B.2. Permanent Gas Analysis Results for Samples Collected from the Headspace of Tank U-112 and for Ambient Air and Ambient Air Through the ISVS Collected near Tank U-112 in SUMMA (TM) Canisters on 7/9/96

Permanent Gas Analyte	Ambient Air Upwind		Ambient Air Through Bundle		Tank Samples						Average		
	S6071-A01.091 ^(a) PNL 091 ^(b) Concentration (ppmv)	<17 <25 376 <17 <17	S6071-A02.092 ^(a) PNL 092 ^(b) Concentration (ppmv)	<17 <25 379 <17 <17	S6071-A04.093 ^(a) PNL 093 ^(b) Concentration (ppmv)	233 <25 <17 <17 394	S6071-A05.183 ^(a) PNL 183 ^(b) Concentration (ppmv)	231 <25 <17 <17 400	S6071-A06.333 ^(a) PNL333 ^(b) Concentration (ppmv)	231 <25 <17 <17 400	S6071-A05.183 ^(a) PNL 183 ^{(b)(c)} Concentration (ppmv)	227 <25 <17 <17 401	Concentration Tank Samples (ppmv)
Hydrogen													
Methane													
Carbon Dioxide													
Carbon Monoxide													
Nitrous Oxide													

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 183; results are not included in the calculation of average concentrations.

Appendix C

Tank Vapor Characterization:

Total Non-Methane Organic Compounds

Appendix C

Tank Vapor Characterization: Total Non-Methane Organic Compounds

C.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant-free according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. The canister is filled a final time with purified humid air for analysis. If the canister is verified as clean by TO-12, the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 µL of distilled water and labeled with a field-sampling identification. Canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

C.2 Analytical Procedure

The SUMMA™ canister samples were analyzed according to PNNL Technical Procedure PNL-TVP-08^(b), which is similar to U.S. Environmental Protection Agency (EPA) compendium Method TO-12. The method detection limits in the sub mg/m³ are required to determine total non-methane organic compounds (TNMOC) concentration in the tank samples.

The method uses an EnTech 7000 cryoconcentration system interfaced with a Hewlett-Packard 5890 gas chromatograph/flame ionization detector (GC/FID). The EnTech concentrator is used to pull a metered volume of 50 to 100 mL of sample air from the SUMMA™ canister mounted on an EnTech 7016CA 16-canister autosampler. The sample is cryogenically concentrated, and constituents are trapped in a stainless steel tube containing glass beads and Tenax. The glass bead/Tenax trap is heated to 180°C and purged with ultra high purity (UHP) helium (He). The purged TNMOCs are carried by a UHP He stream to the GC equipped with an FID where gross organic content is detected and measured.

The GC oven is programmed to run at a 150°C isothermal temperature. Chromatographic separation is not needed in this method since quantitation is from the entire FID response over the run time.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

(b) Pacific Northwest Laboratory. 12/95. *Determination of TO-12 Total Nonmethane Organic Compounds in Hanford Waste Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Flame Ionization Detection*, PNL-TVP-08 (Rev. 1), PNL Technical Procedure, Pacific Northwest Laboratory, Richland, Washington.

Twenty-four hours before the analysis, the SUMMA™ canister samples are pressurized with purified air (supplied by Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. The sample dilution was taken into account when calculating the analysis results.

C.3 Quality Assurance/Quality Control

This method requires user calibration (category 2 measuring and test equipment) of the analytical system in accordance with QA plan ETD-002.

The TNMOC is calibrated by using propane as the calibration standard. The instrument calibration mixture for the PNL-TVP-08 analysis consists of National Institute for Standards and Technology (NIST) 99.999% propane analyzed using a five-point, multi-level, linear regression curve.

A continuing calibration verification (CCV) standard of 100 ppmv propane is analyzed to confirm acceptability of instrument performance. The initial calibration is then used to quantify the samples.

Immediately before running the analysis sequence, a leak-check procedure, which includes evacuating the transfer lines and monitoring the pressure, must be performed on the sample manifold tower. The control limits on this test require that the change in pressure is <1.5 psi, and the absolute pressure after evacuation is <3 psi for each manifold position specified in the sequence table. If this criterion is not met, it must be corrected before the samples are analyzed.

Before the tank samples were analyzed, a diagnostic check was performed on the GC/FID instrument by running a system cleanliness procedure and an instrument continuing calibration as described in PNL-TVP-08. First, two blank volumes of Aadco purified air were analyzed to check the cleanliness of the system. This demonstrates through the analysis of a zero-air blank that the level of interference is acceptable in the analytical system. The system should be cleaned to 0.1 mg/m³ of TNMOCs. Second, an instrument continuing calibration is run using 100-mL UHP propane analyzed using the response factor as an external standard method followed by one blank volume of Aadco air.

C.3.1 Quantitation Results of Target Analytes. The mg/m³ was derived from the five-point multilevel calibration curve from the propane standard using the following equation:

$$\text{mg/m}^3 = \frac{(\text{ng TNMOC}) \times (\text{dilution factor})}{\text{mL sampled volume}} \quad (\text{C.1})$$

The ng/m³ concentrations are calculated from mg/m³ using the equation:

$$\text{ng/m}^3 \text{ TNMOC} = \frac{(\text{ng TNMOC})}{(\text{mL sampled})} \times \text{Dilution Factor} \times \frac{(\text{mg})}{(1 \times 10^6 \text{ mL})} \times \frac{(1 \times 10^6 \text{ mL})}{(\text{m}^3)} \quad (\text{C.2})$$

C.4 Total Non-Methane Organic Compounds Sample Results

Table C.1 lists results of the TO-12 gas analysis from samples collected from the headspace of Tank U-112, ambient air collected ~10 m upwind of the tank, and ambient air collected through the ISVS. Samples were analyzed on August 28, 1996. Concentrations in the ambient air samples were from <0.59 mg/m³. Concentrations in the three tank headspace samples ranged from 1.85 mg/m³ to 2.16 mg/m³ with an average concentration of 2.03 mg/m³. This compares to 6.72 mg/m³ for the sum of all target compounds and TICs identified in the analysis of the SUMMA™ canisters. A replicate analysis was performed on SUMMA™ canister PNL 183; however, only the results from the first analysis are included in the average concentration reported for the tank headspace samples.

A deviation was made to the current procedure (PNL-TVP-08) and documented in Vapor Deviation Reports #JAE082996 and #KLS102496. The following is a discussion of the deviations:

In accordance with the current method past TO-12 analyses used a calibration method based on an average response factor spanning the full dynamic range. Because the low level standards are impacted to some extent by the small amount of system blank always present, the average response factor method generates a large apparent nonlinearity introducing an unnecessary amount of level dependent error. To correct this situation, data included in this and all subsequent calibrations shall use a linear regression fit which includes both a slope and intercept. The correlation coefficient for this ten point calibration curve is 0.99996, an extremely well ordered data set. In conjunction with the change made to use a linear regression fit for calibration, the low level standard will be used as the EQL. Sample results will be flagged with a less-than symbol (<) when below the EQL value. A new revision to procedure PNNL-TVP-08 currently under preparation will reflect these amendments.

Table C.1. TO-12 Results for Samples Collected Through the ISVS from the Headspace of Tank U-112 and from Ambient Air Near Tank U-112 in SUMMA (TM) Canisters on 7/09/96.

TO-12	Ambient Air		Tank Samples				Average Concentration Tank Samples (mg/m ³)
	Upwind	Through Bundle	S6071-A04.093 ^(a)	S6071-A05.183 ^(a)	S6071-A06.333 ^(a)	S6071-A05.183 ^(a)	
	S6071-A01.091 ^(a)	S6071-A02.092 ^(a)	PNL 093 ^(b)	PNL 183 ^(b)	PNL 333 ^(b)	PNL 183 ^(b)	
	Concentration (mg/m ³)						
	<0.59	<0.59	1.85	2.07	2.16	2.05	2.03

Footnotes

- (a) WHC sample identification number.
- (b) PNL canister number.
- (c) Replicate analysis for PNL 183; results are not included in the calculation of average concentrations.

Appendix D

Tank Vapor Characterization:

Organic Analytes by SUMMA™ Method

Appendix D

Tank Vapor Characterization: Organic Analytes by SUMMA™ Method

D.1 Sampling Methodology

Before sending SUMMA™ canisters out to the field for sampling, the canisters are cleaned and verified contaminant free according to Pacific Northwest Laboratory (PNNL) Technical Procedure PNL-TVP-02^(a). The cleaning procedure uses an EnTech 3000 cleaning system that controls 1) filling the canisters with purified humid air and 2) evacuating, for several cycles with applied heat, before allowing the canister to evacuate overnight. If the canister is verified as clean, free of TO-14 and unknown contaminants to a level of 5 parts per billion by volume (ppbv), the canister is evacuated to 5 mtorr, tagged, and stored for use in the field. Before sending the canisters out to the field for sampling, the canister vacuum is measured to determine if any leakage has occurred. If the vacuum has remained constant during storage, the canisters are prehumidified with 100 μ L of distilled water and labeled with a field-sampling identification. Cleaned canisters stored more than 30 but less than 60 days are re-evacuated and rehumidified before use. If stored more than 60 days, the canisters are recleaned and validated before use.

D.2 Analytical Procedure

The SUMMA™ canister sample was analyzed according to PNNL Technical Procedure PNL-TVP-03^(b), which is a modified version of EPA compendium Method TO-14. The method uses EnTech 7000 cryoconcentration systems interfaced with a 5972 Hewlett-Packard benchtop gas chromatograph/mass spectrometer (GC/MS). The EnTech concentrator is used to pull a metered volume of sample air from the SUMMA™ canister, cryogenically concentrate the air volume, then transfer the volume to the GC/MS for analysis. A 100-mL volume of sample is measured and analyzed from the tank headspace. The organic components in the sampled air are separated on an analytical column, J&W Scientific DB-1 phase, 60-m by 0.32-mm internal diameter with 3- μ m film thickness. The GC oven is programmed to run a temperature gradient beginning at 40°C, hold for 5 min, and ramp at 4°C per min to a final temperature of 260°C, with a 5-min hold. Twenty-four hours before the analysis, the SUMMA™ canister samples were pressurized with purified air (supplied by Aadco Instruments, Inc., 1920 Sherwood St., Clearwater, Florida 34625). The starting pressure was first measured using a calibrated diaphragm gauge (Cole Parmer), then pressurized to a level exactly twice the original pressure. For example, if the canister had a starting pressure of 740 torr, it was pressurized to 1480 torr. This dilution was an effort to improve the precision of the analysis. The sample dilution was taken into account when calculating the analysis results.

(a) Pacific Northwest Laboratory. 8/94. *Cleaning SUMMA™ Canisters and the Validation of the Cleaning Process*, PNL-TVP-02 (Rev. 0), PNL Technical Procedure, Richland, Washington.

(b) Pacific Northwest Laboratory. 8/96. *Determination of TO-14 Volatile Organic Compounds in Hanford Tank Headspace Samples Using SUMMA™ Passivated Canister Sampling and Gas Chromatographic-Mass Spectrometric Analysis*, PNL-TVP-03 (Rev. 2), PNL Technical Procedure, Richland, Washington.

The instrument calibration mixture for the PNL-TVP-03 analysis consists of 67 organic analytes. These 67 compounds that are directly quantified in this analysis make up the target analyte list (these 67 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table D.1. The calibration mixture was prepared by blending a commercially prepared TO-14 calibration mixture with a mixture created using a Kin-Tek® permeation-tube standard

Table D.1 Target Organic Analytes

Dichlorodifluoromethane	p/m-Xylene
Chloromethane	1-Ethyl-2-methylbenzene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Styrene
Vinyl Chloride	1,1,2,2-Tetrachloroethane
Bromomethane	o-Xylene
Chloroethane	1,3,5-Trimethylbenzene
Trichlorofluoromethane	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Acetone
1,1,1-Trichloroethane	Acetonitrile
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Chlorobenzene	Propanol
Ethylbenzene	Nonane
Undecane	Dodecane
Tridecane	Tetradecane
Butane	Pentane
1-Butanol	Octane
Methanol	Ethanol
1,3-Butadiene ^(a)	Pentanenitrile
Hexanenitrile	

(a) The low level standard is used as the EQL for these compounds

generation system. The operation of the permeation-tube system follows the method detailed in PNNL Technical Procedure PNL-TVP-06^(a). The standard calibration mix was analyzed using four aliquot sizes ranging from 30 mL to 200 mL, and a response factor for each compound was calculated. The GC/MS response for these compounds has been previously determined to be linearly related to concentration. Instrument detection limits and EQLs have been determined. The compound 1,3-butadiene is not currently included in the method performance section of the procedure for System 2; however, this analyte was analyzed by this method. The low level standard is used as the EQL for this compound. Sample results are flagged with a less-than symbol (<) when less than the EQL.

D.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running an instrument "high-sensitivity tune," as described in PNL-TVP-03. Upon satisfactory completion of the instrument diagnostic check, a blank volume of purified nitrogen was analyzed to check the cleanliness of the system. The instrument was then calibrated using a standard gas mixture containing 67 organic compounds. A gas mixture containing bromochloromethane, 1,4-difluorobenzene, chlorobenzene-d₅, and bromofluorobenzene was used as an internal standard (IS) for all blank, calibration standard, and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. The calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample. Method blanks are analyzed before and after calibration standards and tank headspace samples are analyzed.

D.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated using the average response factors generated using the IS method described above and in PNL-TVP-03. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \quad (\text{D.1})$$

D.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the EPA/National Institute for Standards and Technology (NIST) and WILEY electronic mass spectra libraries. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. This is roughly equivalent to 10 ppbv, depending on the relative response

^(a) Pacific Northwest Laboratory. 11/94. *Preparation of TO-14 Volatile Organic Compounds Gas Standards*, PNL-TVP-06 (Rev. 0). PNL Technical Procedure, Richland, Washington.

factor of the individual TIC as compared with the nearest elution IS. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m^3 :

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (\text{D.2})$$

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound.

The ppbv concentrations are calculated from mg/m^3 and the molecular weight of the analyte.

$$\text{TIC in ppbv} = \frac{\text{TIC (mg/m}^3\text{)} \times 22.4 \text{ L/mol} \times 1000}{\text{TIC g mol wt}} \quad (\text{D.3})$$

All calculated sample concentrations were multiplied by a factor of 2 to account for the dilution step described in Section D.2.

D.4 Organic Sample Results

Five SUMMA™ canisters were returned to the laboratory on July 16, 1996 under WHC COC form 100250 (see Appendix F). Samples were analyzed on September 11, 1996.

The results from the GC/MS analysis of the tank headspace SUMMA™ samples are presented in Table D.2. The results of replicate analyses on a single SUMMA™ canister are presented in Table D.3. The results of the GC/MS analysis of the ambient air sample collected upwind of Tank U-112 and through the ISVS near Tank U-112 are presented in Table D.4.

Table D.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table D.2 were not detected in any of the tank headspace samples above the compound IDL. Fifty-six target analytes above the IDL and four TICs were detected in the tank headspace samples. Fifty-five target analytes and four TICs were identified in two or more tank headspace samples. Methanol at $2.04 \text{ mg}/\text{m}^3$ and ethanol at $1.02 \text{ mg}/\text{m}^3$ accounted for 51% of the target compounds and 46% of the total compounds identified in the analysis. The total concentration of the target analytes was $5.98 \text{ mg}/\text{m}^3$. Propane ($0.19 \text{ mg}/\text{m}^3$) and hexamethylcyclotrisiloxane ($0.40 \text{ mg}/\text{m}^3$) were the two highest concentration TICs found in two or more of the tank headspace samples. The total concentration of TICs identified was $0.74 \text{ mg}/\text{m}^3$. The total concentration of all the compounds identified was $6.72 \text{ mg}/\text{m}^3$. This compares to a total concentration of $2.03 \text{ mg}/\text{m}^3$ identified in the TO-12 analysis of the three tank headspace samples.

SUMMA™ canister PNL 183 was analyzed in replicate for target analytes and TICs to determine analytical precision. Forty-nine of 55 target compounds and three of four TICs had RPDs of less than 10%.

Fifty-five target compounds and one TIC were observed in one or both of the ambient air samples. Many of the compounds were identified at trace levels. Several notable exceptions include methanol at 56 ppbv, acetone at 30 ppbv, and pyridine at 28 ppbv. Trace levels of many of the target analytes may be false positives due to the fact that some of the compounds were found in the CCB above the EQL and are greater than 20 times the concentration found in the sample. These compounds are flagged with a "B" in the tables.

The following procedural changes and observations were noted during the analysis of Tank U-112:

The compound 1,3-butadiene is not currently included in the method performance section of the procedure for System 2; however, this analyte was analyzed by this method. The low level standard is used as the EQL for this compound. Sample results are flagged with a less-than symbol (<) when less than the EQL.

The % RSD for the initial calibration was less than 30% for all target compounds except pyridine (40.9%), decane (35.3%), undecane (44.7%) and tetradecane (49.2%). Pyridine was found at concentrations above the EQL in S6071-A02.092 (ambient through the system), S6071-A05.183 (tank sample), and in the replicate analysis for S6071-A05.183. Decane, undecane, and tetradecane were not found above the EQL in any of the ambient or tank samples.

The percent difference (% D) for the initial calibration verification was less than 25% for all target compounds except 1-butanol (30.4%), pyridine (30.2%), decane (28.6%), undecane (36.6%), dodecane (27.0%), tridecane (31.6%) and tetradecane (51.4%).

The initial calibration blank (ICB) showed evidence of contamination carry-over from the initial calibration verification. The rotor for the 2 position Entech valve was changed following analysis of this ICB and before acquisition of data for Tank U-112. Target compounds exceeding the EQL in a 200 mL ICB were acetonitrile (2.07 ng on column, 5.65 ppbv), acetone (3.64 ng on column, 7.01 ppbv), trichlorofluoromethane (2.26 ng on column, 1.84 ppbv), pentane (1.48 ng on column, 2.30 ppbv), methylene chloride (1.95 ng on column, 2.57 ppbv), 1,1,2-trichloro-1,2,2-trifluoroethane (2.80 ng on column, 1.68 ppbv), 1,1-dichloroethane (1.63 ng on column, 1.84 ppbv), hexane (2.20 ng on column, 2.86 ppbv), chloroform (2.06 ng on column, 1.93 ppbv), tetrahydrofuran (1.45 ng on column, 2.25 ppbv), 1,1,1-trichloroethane (2.21 ng on column, 1.86 ppbv), benzene (1.22 ng on column, 1.75 ppbv), carbon tetrachloride (2.31 ng on column, 1.68 ppbv), trichloroethene (2.18 ng on column, 1.86 ppbv), cis-1,3-dichloropropene (1.43 ng on column, 1.45 ppbv), pyridine (6.20 ng on column, 8.78 ppbv), trans-1,3-dichloropropene (1.41 ng on column, 1.43 ppbv), pentanenitrile (2.72 ng on column, 3.66 ppbv), 1,1,2-trichloroethane (2.20 ng on column, 1.85 ppbv), toluene (1.52 ng on column, 1.85 ppbv), 1,2-dibromoethane (3.18 ng on column, 1.89 ppbv), tetrachloroethylene (2.74 ng on column, 1.85 ppbv), chlorobenzene (2.05 ng on column, 2.04 ppbv), and ethylbenzene (1.79 ng on column, 1.88 ppbv). Note that no target compounds exceeding the EQL were detected at concentrations greater than 5 ppbv with the exception of acetonitrile and acetone.

The % D was less than 25% for all CCV target compounds except

1,2-dichloro-1,1,2,2-tetrafluoroethane (31.8%), methanol (52.7%), vinyl chloride (68.5%), 1,3-butadiene (43.0%), butane (41.8%), bromomethane (108.4%), decane (34.0%), and undecane (44.7%). Of the CCV target compounds exceeding the 25% D, only methanol and butane were found in tank samples above the EQL. Tank samples did not contain 1,2-dichloro-1,1,2,2-tetrafluoroethane, vinyl chloride, 1,3-butadiene, bromomethane, decane, or undecane at concentrations above the EQL. Methanol was found in both ambient samples at concentrations below the EQL and in all tank samples at concentrations above the EQL. Butane was not detected in the ambient upwind sample, was detected at a concentration below the EQL in the ambient sample collected through the system, and was found in all tank samples at concentrations above the EQL.

No target compounds were present in the continuing calibration blank (CCB) above the EQL except methylene chloride (1.30 ng on column, 3.42 ppbv), hexane (1.21 ng on column, 3.15 ppbv), 1,1,1-trichloroethane (1.19 ng on column, 2.00 ppbv), trichloroethene (1.16 ng on column, 1.98 ppbv), cis-1,3-dichloropropene (0.84 ng on column, 1.70 ppbv), and 1,2-dibromoethane (1.57 ng on column, 1.87 ppbv). None of these compounds were present at levels greater than 5 ppbv. Of the target compounds present in the CCB above the EQL, only methylene chloride, hexane, 1,1,1-trichloroethane, trichloroethene, cis-1,3-dichloropropene, and 1,2-dibromoethane were found in either tank or ambient samples.

The upwind ambient sample contained 1,1,1-trichloroethane, trichloroethene, and cis-1,3-dichloropropene above the EQL for these compounds.

The ambient sample through the sampling system contained methylene chloride, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1-dichloroethane, hexane, chloroform, 1,1,1-trichloroethane, benzene, carbon tetrachloride, trichloroethene, cis-1,3-dichloropropene, pyridine, toluene, and 1,2-dibromoethane above the EQL for these compounds.

Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Samples from the Headspace in Tank U-112 in SUMMA Canisters Collected on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A04.093 ^(c) ISVS		S6071-A05.183 ^(c) ISVS		S6071-A06.333 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³)	(ppbv) Flag	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.			
Dichlorodifluoromethane	75-71-8	121	4.9	0.029	5.4	J	0.028	5.3	J	0.031	5.8	J	0.030	0.001	5.5	0.28
Chloromethane	74-87-3	50	4.6	0.013	5.9	J	0.013	5.9	J	0.016	6.9	J	0.014	0.001	6.2	0.57
1,2-dichloro 1,1,2,2-tetrafluoroethane	76-14-2	171	4.9	0.041	5.4	J	0.040	5.3	J	0.045	5.9	J	0.042	0.002	5.5	0.32
Methanol	67-56-1	32	5.1	2.038	1425		2.108	1473		1.980	1384		2.042	0.064	1427	45
Vinyl Chloride	75-01-4	63	5.2	0.017	6.0	J	0.017	6.0	J	0.019	6.8	J	0.017	0.001	6.2	0.45
Butane	106-97-8	58	5.6	0.113	43		0.118	45		0.122	47		0.118	0.005	45	1.9
Chloroethane	75-00-3	65	6.6	0.016	5.5	J	0.016	5.6	J	0.017	6.0	J	0.016	0.001	5.7	0.28
Ethanol	64-17-5	46	6.9	1.015	494		1.063	518		0.976	475		1.018	0.044	496	22
Acetonitrile	75-05-8	41	7.4	0.048	26		0.039	21		0.043	23		0.043	0.005	24	2.5
Acetone	67-64-1	58	7.9	0.172	66		0.179	69		0.205	79		0.185	0.017	71	7
Trichlorofluoromethane	75-69-4	137	8.3	0.540	88		0.563	92		0.576	94		0.560	0.018	91	3.0
Pentane	109-66-0	72	9.0	0.040	12		0.041	13		0.044	14		0.042	0.002	13	0.62
1,1-Dichloroethene	75-35-4	97	9.6	0.020	4.6	J	0.022	5.2	J	0.021	4.8	J	0.021	0.001	4.8	0.31
Methylene Chloride	75-09-2	85	9.8	0.030	8.0	B	0.030	8.0	B	0.033	8.6	B	0.031	0.001	8.2	0.33
1,1,2-Trichloroethane	76-13-1	187	10.4	0.095	11		0.081	9.7		0.087	10		0.087	0.007	10	0.83
Propanenitrile	107-12-0	55	11.2	0.032	13	J	0.033	13	J	0.039	16	J	0.035	0.003	14	1.4
Propanol	71-23-8	60	11.3	0.071	26		0.070	26		0.067	25		0.069	0.002	26	0.68
1,1-Dichloroethane	75-34-3	99	12.1	0.022	5.0		0.022	5.0		0.025	5.6		0.023	0.001	5.2	0.32
cis-1,2-Dichloroethene	156-59-2	97	13.7	0.020	4.5	J	0.019	4.5	J	0.021	4.8	J	0.020	0.001	4.6	0.18
Hexane	110-54-3	86	14.1	0.046	12	B	0.047	12	B	0.050	13	B	0.048	0.002	12	0.59
Chloroform	67-66-3	119	14.3	0.027	5.1		0.027	5.0		0.029	5.5		0.028	0.001	5.2	0.25
Tetrahydrofuran	109-99-9	72	15.0	0.057	18		0.060	19		0.062	19		0.060	0.002	19	0.75
1,1,1-Trichloroethane	71-55-6	133	16.2	0.050	8.4	B	0.050	8.4	B	0.053	9.0	B	0.051	0.002	8.6	0.34
1-Butanol	71-36-3	74	16.9	0.233	70		0.225	68		0.216	65		0.225	0.008	68	2.6
Benzene	71-43-2	78	17.1	0.028	7.9		0.028	7.9		0.031	8.8		0.029	0.002	8.2	0.53
Carbon Tetrachloride	56-23-5	154	17.4	0.038	5.5		0.039	5.6		0.042	6.1		0.039	0.002	5.7	0.28
Trichloroethene	79-01-6	131	19.2	0.027	4.7	B	0.028	4.9	B	0.030	5.1	B	0.029	0.001	4.9	0.22
Heptane	142-82-5	100	19.8	0.030	6.8	J	0.030	6.8	J	0.032	7.2	J	0.031	0.001	6.9	0.24
cis-1,3-Dichloropropene	10061-01-5	111	20.9	0.020	4.0	B	0.000	0.04	U	0.021	4.3	B	0.021	e	4.1	e
4-Methyl-2-Pentanone	108-10-1	100	21.0	0.039	8.7	J	0.121	27		0.043	9.7	J	0.068	0.046	15	10
Pyridine	110-86-1	79	21.1	0.040	11	J	0.127	36		0.031	8.9	J	0.066	0.053	19	15
trans-1,3-Dichloropropene	10061-02-6	111	22.0	0.020	4.1	J	0.020	4.1	J	0.022	4.5	J	0.021	0.001	4.2	0.20
Pentanenitrile	110-59-8	83	22.1	0.033	8.9	J	0.033	9.0	J	0.038	10	J	0.035	0.003	9.4	0.69
1,1,2-Trichloroethane	79-00-5	133	22.5	0.027	4.5	J	0.028	4.7	J	0.028	4.8		0.028	0.001	4.6	0.14
Toluene	108-88-3	92	23.1	0.209	51		0.215	52		0.215	52		0.213	0.003	52	0.82
1,2-Dibromoethane	106-93-4	188	24.6	0.035	4.1	B	0.035	4.1	B	0.037	4.4	B	0.035	0.001	4.2	0.16
Octane	111-65-9	114	25.2	0.019	3.7	J	0.019	3.7	J	0.019	3.8	J	0.019	0.000	3.7	0.081
Tetrachloroethylene	127-18-4	166	25.6	0.039	5.3		0.040	5.4		0.041	5.5		0.040	0.001	5.4	0.14

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Table D.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Samples from the Headspace in Tank U-112 in SUMMA Canisters Collected on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time (min)	S6071-A04.093 ^(c) ISVS		S6071-A05.183 ^{(c)(d)} ISVS		S6071-A06.333 ^(c) ISVS		Mean and Standard Deviation		
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St. Dev.	(ppbv)
Chlorobenzene	108-90-7	113	27.2	0.023	4.6	0.028	5.6	0.025	5.0	0.025	5.0	0.49
Hexanenitrile	628-73-9	97	27.6	0.032	7.3	0.031	7.1	0.037	8.5	0.033	7.6	0.75
Ethylbenzene	100-41-4	106	28.1	0.026	5.4	0.026	5.5	0.027	5.7	0.026	5.5	0.16
p/m-Xylene	106-42-3	106	28.6	0.053	11	0.057	12	0.056	12	0.055	12	0.43
Cyclohexanone	108-94-1	98	29.0	0.021	4.7	0.026	5.9	0.020	4.7	0.022	5.1	0.68
Styrene	100-42-5	104	29.5	0.018	3.8	0.018	3.8	0.019	4.0	0.018	3.9	0.11
1,1,2,2-Tetrachloroethane	79-34-5	168	29.7	0.034	4.5	0.034	4.5	0.037	4.9	0.035	4.7	0.21
o-Xylene	95-47-6	106	29.8	0.025	5.4	0.026	5.5	0.026	5.4	0.026	5.4	0.091
Nonane	111-84-2	128	30.3	0.019	3.2	0.018	3.2	0.021	3.7	0.019	3.4	0.29
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.2	0.023	4.2	0.023	4.2	0.022	4.1	0.023	4.2	0.04
1,3,5-Trimethylbenzene	108-67-8	120	33.4	0.020	3.7	0.020	3.7	0.020	3.7	0.020	3.7	0.02
1,2,4-Trimethylbenzene	95-63-6	120	34.6	0.022	4.1	0.022	4.1	0.022	3.7	0.022	4.0	0.22
Decane	124-18-5	142	34.9	0.045	7.0	0.044	6.9	0.049	7.8	0.046	7.2	0.46
Hexachloro-1,3-butadiene	87-68-3	261	44.5	0.034	2.9	0.035	3.0	0.036	3.1	0.035	3.0	0.10

Tentatively Identified Compounds^(b)

Propane	74-98-6	44	4.1	0.274	139	N	0.142	72	N	0.147	75	N	0.188	0.075	95	38
Isopropyl Alcohol	67-63-0	60	8.5	0.150	56	N	0.156	58	N	0.148	55	N	0.151	0.004	56	1.6
Methane, nitro-	75-52-5	61	10.6	nd	nd	nd	nd	nd	nd	0.144	53	N	e	e	e	e
Cyclotrisiloxane, hexamethyl-	541-05-9	222	26.1	0.119	12	N	0.136	14	N	0.939	95	N	0.398	0.469	40	47

Data Quality Flags

- B Compound found in associated laboratory blank.
- J Target compound detected above the IDL but below the EQL.
- N Denotes tentatively identified compound
- U Flag denotes compound not detected above listed IDL

Footnotes

- (a) Detected target analytes.
- (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
- (c) WHC sample identification number.
- (d) Replicates of this sample are found in Table D.3.
- (e) Mean and/or standard deviation are not meaningful for this analyte.
- (f) No molecular weight available for calculation.

nd Not detected

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single SUMMATM Canister Collected from the Headspace of Tank U-112 on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A05.183 ^(c)						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Dichlorodifluoromethane	75-71-8	121	4.9	0.028	5.3	J	0.030	5.6	J	5
Chloromethane	74-87-3	50	4.6	0.013	5.9	J	0.015	6.6	J	11
1,2-dichloro 1,1,2,2-tetrafluoroethane	76-14-2	171	4.9	0.040	5.3	J	0.044	5.7	J	9
Methanol	67-56-1	32	5.1	2.108	1473		2.111	1476		0
Vinyl Chloride	75-01-4	63	5.2	0.017	6.0	J	0.018	6.5	J	9
Butane	106-97-8	58	5.6	0.118	45		0.122	47		3
Chloroethane	75-00-3	65	6.6	0.016	5.6	J	0.017	5.8	J	4
Ethanol	64-17-5	46	6.9	1.063	518		1.063	518		0
Acetonitrile	75-05-8	41	7.4	0.039	21		0.041	23		6
Acetone	67-64-1	58	7.9	0.179	69		0.180	69		0
Trichlorofluoromethane	75-69-4	137	8.3	0.563	92		0.574	94		2
Pentane	109-66-0	72	9.0	0.041	13		0.044	14		6
1,1-Dichloroethene	75-35-4	97	9.6	0.022	5.2	J	0.024	5.7	J	9
Methylene Chloride	75-09-2	85	9.8	0.030	8.0	B	0.032	8.3	B	4
1,1,2-trichloro 1,1,2,2-trifluoroethane	76-13-1	187	10.4	0.081	9.7		0.083	10.0		3
Propanenitrile	107-12-0	55	11.2	0.033	13	J	0.035	14	J	6
Propanol	71-23-8	60	11.3	0.070	26		0.072	27		2
1,1-Dichloroethane	75-34-3	99	12.1	0.022	5.0		0.024	5.5		10
cis-1,2-Dichloroethene	156-59-2	97	13.7	0.019	4.5	J	0.021	4.8	J	7
Hexane	110-54-3	86	14.1	0.047	12	B	0.049	13	B	5
Chloroform	67-66-3	119	14.3	0.027	5.0		0.029	5.5		9
Tetrahydrofuran	109-99-9	72	15.0	0.060	19		0.061	19		1
1,1,1-Trichloroethane	71-55-6	133	16.2	0.050	8.4	B	0.052	8.8	B	5
1-Butanol	71-36-3	74	16.9	0.225	68		0.240	73		6
Benzene	71-43-2	78	17.1	0.028	7.9		0.029	8.4		5
Carbon Tetrachloride	56-23-5	154	17.4	0.039	5.6		0.041	5.9		5
Trichloroethene	79-01-6	131	19.2	0.028	4.9	B	0.030	5.2	B	6
Heptane	142-82-5	100	19.8	0.030	6.8	J	0.031	7.0	J	4
4-Methyl-2-Pentanone	108-10-1	100	21.0	0.121	27		0.124	28		2
Pyridine	110-86-1	79	21.1	0.127	36		0.146	41		14
trans-1,3-Dichloropropene	10061-02-6	111	22.0	0.020	4.1	J	0.022	4.5	J	8
Pentanenitrile	110-59-8	83	22.1	0.033	9.0	J	0.036	9.7	J	8
1,1,2-Trichloroethane	79-00-5	133	22.5	0.028	4.7	J	0.029	4.9		4
Toluene	108-88-3	92	23.1	0.215	52		0.220	54		2
1,2-Dibromoethane	106-93-4	188	24.6	0.035	4.1	B	0.037	4.4	B	6
Octane	111-65-9	114	25.2	0.019	3.7	J	0.019	3.8	J	4
Tetrachloroethylene	127-18-4	166	25.6	0.040	5.4		0.042	5.6		5
Chlorobenzene	108-90-7	113	27.2	0.028	5.6		0.030	5.9		5
Hexanenitrile	628-73-9	97	27.6	0.031	7.1	J	0.035	8.0	J	12
Ethylbenzene	100-41-4	106	28.1	0.026	5.5	J	0.027	5.7	J	4
p/m-Xylene	106-42-3	106	28.6	0.057	12	J	0.060	13	J	5
Cyclohexanone	108-94-1	98	29.0	0.026	5.9	J	0.027	6.3	J	6
Styrene	100-42-5	104	29.5	0.018	3.8	J	0.019	4.0	J	5
1,1,2,2-Tetrachloroethane	79-34-5	168	29.7	0.034	4.5	J	0.036	4.8	J	5
o-Xylene	95-47-6	106	29.8	0.026	5.5	J	0.028	5.9	J	6
Nonane	111-84-2	128	30.3	0.018	3.2	J	0.020	3.4	J	7
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.2	0.023	4.2	J	0.025	4.6	J	8

Table D.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single SUMMATM Canister Collected from the Headspace of Tank U-112 on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A05.183 ^(c)						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
1,3,5-Trimethylbenzene	108-67-8	120	33.4	0.020	3.7	J	0.022	4.0	J	7
1,2,4-Trimethylbenzene	95-63-6	120	34.6	0.022	4.1	J	0.024	4.4	J	9
Decane	124-18-5	142	34.9	0.044	6.9	J	0.046	7.2	J	4
Hexachloro-1,3-butadiene	87-68-3	261	44.5	0.035	3.0	J	0.038	3.2	J	7
Tentatively Identified Compounds^(b)										
Propane	74-98-6	44	4.1	0.142	72	N	0.144	73	N	2
Isopropyl Alcohol	67-63-0	60	8.5	0.156	58	N	0.153	57	N	2
Cyclotrisiloxane, hexamethyl-	541-05-9	222	26.1	0.136	14	N	0.139	14	N	2

Data Quality Flags

- B Compound found in associated laboratory blank.
- J Target compound detected above the IDL but below the EQL.
- N Denotes tentatively identified compound
- U Flag denotes compound not detected above listed IDL

Footnotes

- (a) Detected target analytes.
- (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
- (c) WHC sample identification number.
- (d) Relative percent differences (RPDs) based on mg/m³ values.
- nd Not detected

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank U-112 in SUMMATM Canisters on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A01.091 ^(c)			S6071-A01.092 ^(c)		
				Upwind Ambient Air		Flag	Ambient Air Through Bundle		Flag
				(mg/m ³)	(ppbv)		(mg/m ³)	(ppbv)	
Dichlorodifluoromethane	75-71-8	121	4.9	0.016	2.9	J	0.032	5.8	J
Chloromethane	74-87-3	50	4.6	0.008	3.7	J	0.015	6.4	J
1,1,2,2-tetrafluoroethane	76-14-2	171	4.9	0.022	2.9	J	0.043	5.6	J
Methanol	67-56-1	32	5.1	0.073	51	J	0.080	56	J
Vinyl Chloride	75-01-4	63	5.2	0.009	3.1	J	0.016	5.8	J
Butane	106-97-8	58	5.6	0.008	2.9	U	0.030	11	J
Chloroethane	75-00-3	65	6.6	0.009	3.0	J	0.016	5.5	J
Ethanol	64-17-5	46	6.9	0.029	14	J	0.038	18	J
Acetonitrile	75-05-8	41	7.4	0.018	9.6	J	0.032	17	J
Acetone	67-64-1	58	7.9	0.006	2.3	U	0.006	2.3	U
Trichlorofluoromethane	75-69-4	137	8.3	0.019	3.0	J	0.034	5.6	J
Pentane	109-66-0	72	9.0	0.011	3.5	J	0.022	6.9	J
1,1-Dichloroethene	75-35-4	97	9.6	0.011	2.5	J	0.020	4.7	J
Methylene Chloride	75-09-2	85	9.8	0.022	5.9	B,J	0.031	8.1	B
1,1,2,2-trifluoroethane	76-13-1	187	10.4	0.021	2.5	J	0.221	26	
Propanenitrile	107-12-0	55	11.2	0.018	7.4	J	0.032	13	J
Propanol	71-23-8	60	11.3	0.018	6.7	J	0.039	14	J
1,1-Dichloroethane	75-34-3	99	12.1	0.013	2.9	J	0.022	5.1	
cis-1,2-Dichloroethene	156-59-2	97	13.7	0.012	2.7	J	0.019	4.5	J
Hexane	110-54-3	86	14.1	0.018	4.8	B,J	0.032	8.3	B
Chloroform	67-66-3	119	14.3	0.016	3.0	J	0.027	5.0	
Tetrahydrofuran	109-99-9	72	15.0	0.013	4.0	J	0.022	6.8	J
1,1,1-Trichloroethane	71-55-6	133	16.2	0.019	3.1	B	0.031	5.2	B
1-Butanol	71-36-3	74	16.9	0.020	5.9	J	0.059	18	J
Benzene	71-43-2	78	17.1	0.010	2.8	J	0.017	4.9	
Carbon Tetrachloride	56-23-5	154	17.4	0.019	2.7	J	0.032	4.6	
Trichloroethene	79-01-6	131	19.2	0.017	2.9	B	0.028	4.8	B
Heptane	142-82-5	100	19.8	0.012	2.7	J	0.020	4.5	J
cis-1,3-Dichloropropene	10061-01-5	111	20.9	0.012	2.4	B	0.020	4.0	B
4-Methyl-2-Pentanone	108-10-1	100	21.0	0.022	4.8	J	0.040	9.0	J
Pyridine	110-86-1	79	21.1	0.008	2.2	U	0.008	2	U
trans-1,3-Dichloropropene	10061-02-6	111	22.0	0.003	0.57	U	0.021	4.2	J
Pentanenitrile	110-59-8	83	22.1	0.021	5.6	J	0.037	9.9	J
1,1,2-Trichloroethane	79-00-5	133	22.5	0.017	2.8	J	0.028	4.6	J
Toluene	108-88-3	92	23.1	0.012	2.8	J	0.026	6.3	
1,2-Dibromoethane	106-93-4	188	24.6	0.022	2.6	B,J	0.036	4.3	B
Octane	111-65-9	114	25.2	0.010	1.9	J	0.015	3.0	J
Tetrachloroethylene	127-18-4	166	25.6	0.018	2.5	J	0.030	4.0	J
Chlorobenzene	108-90-7	113	27.2	0.014	2.8	J	0.024	4.7	J
Hexanenitrile	628-73-9	97	27.6	0.021	4.8	J	0.035	8.0	J
Ethylbenzene	100-41-4	106	28.1	0.013	2.8	J	0.022	4.6	J
p/m-Xylene	106-42-3	106	28.6	0.026	5.4	J	0.044	9.3	J
Cyclohexanone	108-94-1	98	29.0	0.015	3.5	J	0.033	7.5	J
Styrene	100-42-5	104	29.5	0.011	2.3	J	0.019	4.1	J
1,1,2,2-Tetrachloroethane	79-34-5	168	29.7	0.022	3.0	J	0.036	4.8	J
o-Xylene	95-47-6	106	29.8	0.013	2.6	J	0.021	4.5	J

Table D.4. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) in Ambient Air and Ambient Air Through the ISVS Collected Near Tank U-112 in SUMMATM Canisters on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A01.091 ^(c)			S6071-A01.092 ^(c)		
				Upwind Ambient Air		Flag	Ambient Air Through Bundle		Flag
				(mg/m ³)	(ppbv)		(mg/m ³)	(ppbv)	
Nonane	111-84-2	128	30.3	0.011	1.9	J	0.016	2.9	J
1-Ethyl-2-Methyl-Benzene	611-14-3	120	33.2	0.022	4.0	U	0.023	4.4	J
1,3,5-Trimethylbenzene	108-67-8	120	33.4	0.017	3.2	U	0.020	3.8	J
1,2,4-Trimethylbenzene	95-63-6	120	34.6	0.020	3.7	U	0.022	4.1	J
Decane	124-18-5	142	34.9	0.015	2.4	J	0.039	6.1	J
Hexachloro-1,3-butadiene	87-68-3	261	44.5	0.023	2.0	U	0.035	3.0	J

Tentatively

Identified Compounds^(b)

Cyclotrisiloxane, hexamethyl-	541-05-9	222	26.1	nd	nd		0.287	29	N
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Data Quality Flags

B Compound found in associated laboratory blank.

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Flag denotes compound not detected above listed IDL

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

nd Not detected

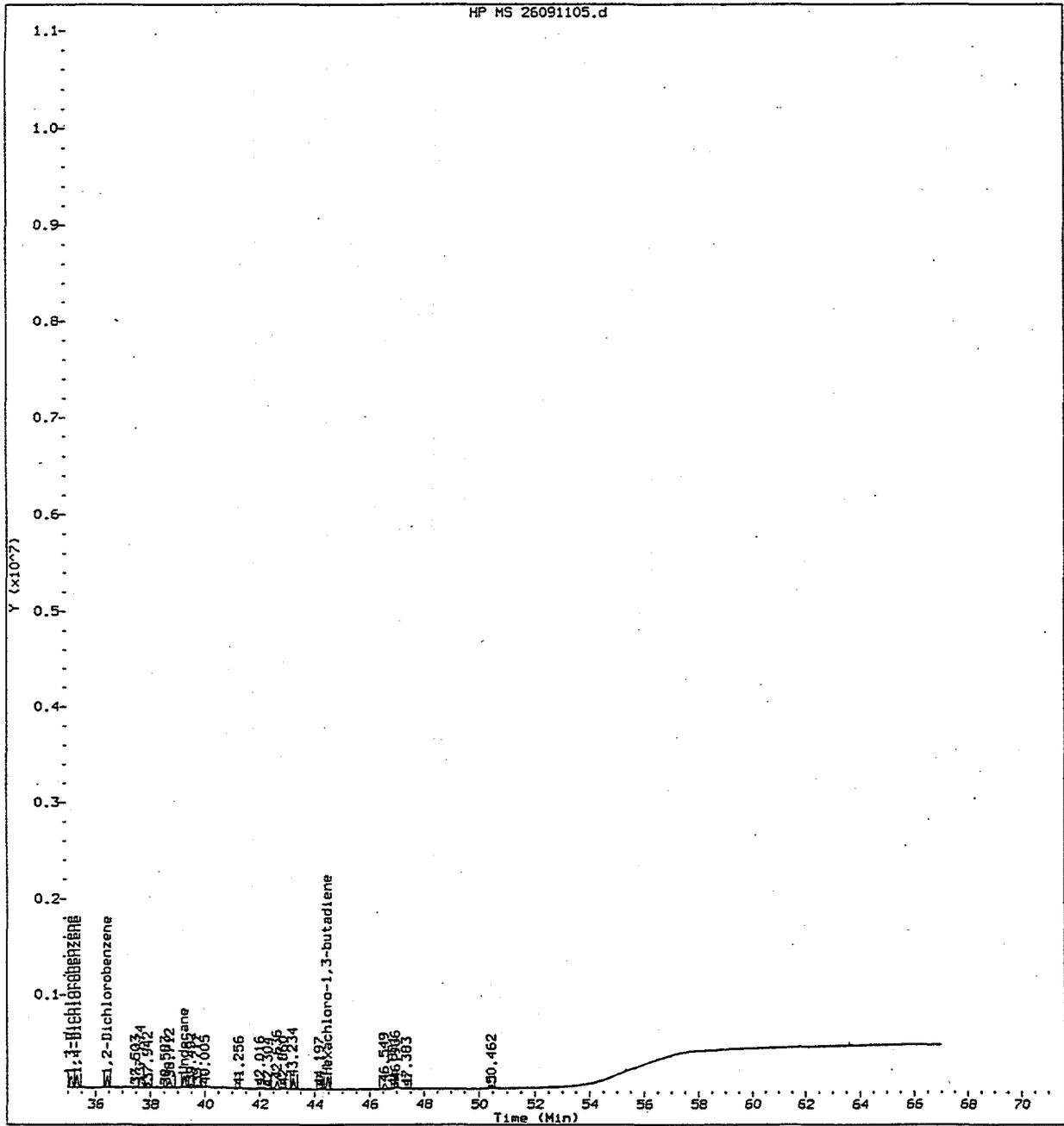


Figure D.1b Total Ion Chromatogram (36 - 70 min) for Hanford Waste Tank U-112
SUMMA™ Canister Sample S6071-A01-092 Collected on 7/9/96

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

Appendix E

Tank Vapor Characterization: Organic Analytes by Triple Sorbent Trap Method

E.1 Sampling Methodology

Samples are collected on Supelco 300 graphite based triple sorbent traps (TST). Before field deployment, each trap is heated to 380°C under inert gas flow for a minimum of 60 min. Tubes are prepared in batches with each tank sampling job constituting one batch. One tube is selected from each batch and run immediately to verify cleanliness. All remaining tubes in the batch receive equal amounts of 3 surrogate compounds (hexafluorobenzene, toluene-d8, and bromobenzene-d5). One per batch tube is run immediately to verify successful addition of surrogate spikes to that batch. Tubes are then placed in individually labeled plastic shipping tubes (Supelco TD³), which are sealed with gasketed end caps, thus providing a rugged, headspace-free shipping and storage medium. As a precautionary measure, sample tubes are kept in refrigerated storage before and after sampling.

E.2 Analytical Procedure

The Supelco 300 tubes were analyzed according to Pacific Northwest National Laboratory (PNNL) Technical Procedure PNL-TVP-10^(a), with the exceptions noted in Section E.4. The method employs Supelco Carbotrap™ 300 traps for sample collection and preconcentration. The traps are ground-glass tubes (11.5 cm long X 6 mm OD, 4 mm ID) containing a series of sorbents arranged in order of increasing retentivity. Each trap contains 300 mg of Carbotrap™ C, 200 mg of Carbotrap™ B, and 125 mg of Carbosieve™ S-III. The first 2 sorbents are deactivated graphite with limited sorption power for less volatile compounds. The final trapping stage, the Carbosieve™ S-III, is a graphitized molecular sieve used to retain the most volatile components, including some permanent gases such as Freon-12. Following sample collection and addition of internal standard (IS), the traps are transferred to a Dynatherm ACEM 900 thermal desorber unit for analysis. The trap on the ACEM 900 is then desorbed by ballistic heating to 350°C with the sample then transferred to a smaller focusing trap. A 10:1 split is used during the transfer with 10% of the sample analyzed and the rest retained for reanalysis. The split sample collected on a second identical Carbotrap™ 300 trap is used for repeat analysis on at least one sample per batch. Since the IS also follows the same path, quantitation may be performed directly on the repeat run without changing the calibration. Following desorption from the Carbotrap™ 300 trap, the analyte is transferred to a long, thin focusing trap filled with the same type of trapping materials as the Carbotrap™ 300 traps and in approximately the same ratios. The purpose of the focusing trap is to provide an interface to a capillary gas chromatography (GC) column, which may be thermally desorbed at a helium (He) flow rate compatible with the column and mass spectrometry (MS) interface (1.2 mL/min). The focusing trap is

^(a) Pacific Northwest Laboratory. 2/96. *Determination of Volatile Organic Compounds in Hanford Waste Tank Headspace Samples Using Triple Sorbent Trap Sampling and Gas Chromatograph-Mass Spectrometer Analysis*, PNL-TVP-10 (Rev. 2), PNL Technical Procedure, Richland, Washington.

ballistically heated to thermally desorb components onto a capillary GC column. The column is subsequently temperature programmed to separate the method analytes, which are then detected by MS.

The instrument calibration mixture for the TST analysis consists of 65 compounds. These 65 compounds that are directly quantified in this analysis make up the target analyte list (these 65 compounds will be referred to as target analytes). A summary of the target analytes is provided in Table E.1. The calibration mixture is prepared in common with the mixture used for the SUMMA™ analysis (see Section D.2). The standard calibration mix was analyzed using 4 aliquot sizes ranging from 100 mL to 1200 mL, and a response factor for each compound was calculated. Volumes of standard added to the traps are measured by pressure difference on a SUMMA™ canister of known volume. The GC/MS response for these compounds has been previously determined to be linearly

Table E.1 Target Organic Analytes

<i>Dichlorodifluoromethane</i>	p/m-Xylene
<i>Chloromethane</i>	Styrene
<i>1,2-Dichloro-1,1,2,2-tetrafluoroethane</i>	1,1,2,2-Tetrachloroethane
<i>Vinyl Chloride</i>	o-Xylene
<i>Chloroethane</i>	1,3,5-Trimethylbenzene
<i>Trichlorofluoromethane</i>	1,2,4-Trimethylbenzene
1,1-Dichloroethene	1,3-Dichlorobenzene
Methylene Chloride	1,4-Dichlorobenzene
1,1,2-Trichloro-1,2,2-trifluoroethane	1,2-Dichlorobenzene
1,1-Dichloroethane	1,2,4-Trichlorobenzene
cis-1,2-Dichloroethene	Hexachloro-1,3-butadiene
Chloroform	2-Butanone
1,2-Dichloroethane	Chlorobenzene
1,1,1-Trichloroethane	<i>Acetonitrile</i>
Benzene	Heptane
Carbon Tetrachloride	Tetrahydrofuran
1,2-Dichloropropane	Pyridine
Trichloroethene	Butanenitrile
cis-1,3-Dichloropropene	Cyclohexane
trans-1,3-Dichloropropene	Decane
1,1,2-Trichloroethane	Hexane
Toluene	4-Methyl-2-pentanone
1,2-Dibromoethane	Propanenitrile
Tetrachloroethylene	Cyclohexanone
Ethylbenzene	Propanol
Tetradecane	Methanol ^(a)
Butane	Ethanol ^(a)
<i>Acetone</i>	Pentane
1-Butanol	Pentanenitrile
Octane	Hexanenitrile
Nonane	2-Ethyl-2-methyl benzene
Undecane	Dodecane
Tridecane	

(a) The low level standard is used as the EQL for these compounds.

Note: Compounds shown in italics have an exceptionally high volatility. They are routinely included in the standard and are quantified, but have a restricted linear dynamic range because of the potential for trap breakthrough.

related to concentration. Instrument detection limits and EQLs have been determined. Methanol and ethanol are not currently included in procedure PNL-TVP-10; however, both compounds were analyzed per this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL.

E.3 Quality Assurance/Quality Control

Before the tank sample was analyzed, a diagnostic check was performed on the GC/MS instrument by running a full auto tune, as described in PNL-TVP-10. Upon satisfactory completion of the instrument diagnostic check, a blank tube was analyzed to check the cleanliness of the system. The instrument was then calibrated using a 300-mL volume of standard gas mixture containing 65 compounds shown in Table E.1. A gas mixture containing difluorobenzene, chlorobenzene-d₅, and 1,4 bromofluorobenzene was used as an IS¹ for all calibration standard and sample analyses. Analyte responses from sample components, ISs, and standards were obtained from the extracted ion plot from their selected mass ion. A continuing calibration was generated by calculating the relative response ratios of the IS to calibration standard responses and plotting the ratios against the ratio of the calibration-standard concentration (in ppbv) to the IS concentration. Once it is determined that the relative response is linear with increasing concentration, an average response factor is calculated for each target analyte and used to determine the concentration of target compounds in each sample.

E.3.1 Quantitation Results of Target Analytes. The quantitative-analysis results for the target analytes were calculated directly from the calibration curve generated using the IS method described above and in PNL-TVP-10. The conversion from ppbv to mg/m³ assumes standard temperature and pressure (STP) conditions of 760 torr and 273K and was calculated directly from the following equation:

$$\text{mg/m}^3 = \frac{(\text{ppbv}/1000) \times \text{g mol wt of compound}}{22.4 \text{ L/mol}} \quad (\text{E.1})$$

E.3.2 Identification and Quantitation of Tentatively Identified Compounds. The tentatively identified compounds (TICs) are determined by mass-spectral interpretation and comparison of the spectra with the U.S. Environmental Protection Agency (EPA)/National Institute for Standards and Technology (NIST) and WILEY Libraries, which are a part of the Hewlett-Packard 5971/5972 instrument operating system. Chromatographic peaks with an area count greater than, or equal to, one-tenth of the total area count of the nearest eluting IS are tentatively identified and quantitatively estimated. The quality of the mass-spectral searches was then reviewed by the principal investigators before the identification was assigned to each chromatographic peak.

The concentration of each TIC was estimated using a relative response factor calculated using the total peak area for the nearest eluting IS. The IS peak area was used to calculate a response factor using the IS concentration in mg/m³:

$$\text{Response Factor} = \frac{\text{IS conc. (mg/m}^3\text{)}}{\text{IS peak area}} \quad (\text{E.2})$$

The calculated response factor was then multiplied by the TIC peak area to give an estimated concentration for that compound.

The ppbv concentrations are calculated from mg/m³ and the molecular weight of the analyte.

$$\text{TIC in ppbv} = \frac{\text{TIC (mg/m}^3\text{)} \times 22.4 \text{ L/mol} \times 1000}{\text{TIC g mol wt}} \quad (\text{E.3})$$

E.4 Organic Sample Results

Eight triple sorbent traps consisting of 4 samples, 2 field blanks and 2 trip blanks were returned to the laboratory on July 16, 1996 under WHC COC form 100251. Samples were analyzed on July 18 and 19, 1996.

The results from the GC/MS analysis of the tank headspace TST samples are presented in Table E.2. The results of replicate analyses on a single TST are presented in Table E.3.

Table E.2 lists the quantitative results for compounds listed as target analytes and TICs. Target compounds not listed in Table E.2 were not detected in any of the tank headspace samples above the compound IDL. Forty-four target analytes above the IDL and 20 TICs were detected in the tank headspace samples. All 44 of the target analytes and 20 TICs were observed in two or more sorbent traps. Methanol at 1.08 mg/m³ and toluene at 0.99 mg/m³ accounted for 38% of the target analytes and 15% of the total concentration identified by the analysis. The total concentration of the target analytes was 5.42 mg/m³ or 39% of the total concentration identified by the analyses. The predominant TICs observed in these samples were 2,4-dimethylheptane at 1.34 mg/m³ and hexamethylcyclotrisiloxane at 1.12 mg/m³. The total concentration of the TICs was 8.56 mg/m³ or 61% of the total concentration identified by analysis. The total concentration of all the compounds identified was 13.98 mg/m³.

Triple sorbent trap sample PNL 1091 was analyzed in replicate for target analytes and TICs to determine analytical precision. Thirty-one of 43 target compounds and 17 of 19 TICs had RPDs of less than 10%.

The following procedural changes and observations were noted during the analysis of Tank U-112:

The field blanks are badly contaminated with a group of compounds characteristic of the 3M adhesive tape used on previous ISVS jobs. Because of the tape problem and other

environmental blank problems incurred during sampling, tank results from this sampling activity should be generally considered as suspect.

Methanol and ethanol are not currently included in procedure PNL-TVP-10; however, both compounds were analyzed per this method. The low level standard is used as the EQL for these compounds. Sample results are flagged with a less-than symbol (<) when less than the EQL value.

Tributyl phosphate (TBP) is included in the analysis target list based on a calibration performed on January 5 and 9, 1996. The TBP was introduced onto a series of double sorbent traps as a methanolic solution standard rather than a vapor standard. This served to determine the retention time and verify the mass spectral characteristics of the compound. However, verification of the calibration acceptability was not performed because the compound is not present in the CCV. At present, it is not possible to prepare a gas standard from this material. The calibration information on TBP demonstrated that detectability at 0.8 ppbv (based on 200 mL sample) was possible. Tributyl phosphate was not detected in the tank samples.

Field blanks, trip blanks, and samples contained minor amounts of 1-chloro,1,1-difluoroethane. This compound has appeared persistently in most samples sent to the field in the past, including blanks. It is believed to be a fugitive refrigerant. That material is never present in tubes archived for a similar amount of time in the 326 Vapor Lab or 329 Building temporary storage. The origin of the material is unclear but since it has shown up in trip blanks as well as field blanks, the most likely candidate is one of the refrigerators used for interim storage.

Very narrow air spikes (mass 32) occasionally are present in chromatograms from this period. This problem has been traced to high frequency air bursts from the surface of MS vacuum system o-rings. Attempts at permanently eliminating this problem have been unsuccessful to date, and the matter has been referred to Hewlett Packard for further investigation. It has no known impact on data quality but the spikes do appear as features on the total ion chromatogram.

Batch 7/18/96:

Samples included in this batch consisted of the two field blanks and two trip blanks.

The field blanks are badly contaminated with a group of compounds at least some of which are characteristic of the 3M adhesive tape used on previous ISVS jobs. Because of the tape problem and other environmental blank problems incurred during sampling, tank results from this sampling activity should generally be considered as suspect.

The CCV showed acceptable performance as specified in the procedure for all target compounds except decane (32%), undecane (25%), dodecane (27%), tridecane (43%), and tetradecane (69%).

The field blanks contained numerous target compounds at levels in excess of the EQL including acetone, **propanol**, **propanenitrile**, **2-butanone**, hexane, **tetrahydrofuran**,

butanenitrile, 1-butanol, cyclohexane, heptane, **4-methyl-2-pentanone**, pentanenitrile, toluene, ethylbenzene, p/m xylene, styrene, o-xylene, and decane. Compounds shown in bold were also seen in the trip blanks at levels in excess of the EQL and were apparently introduced onto the tubes inadvertently during laboratory preparation prior to field sampling. No TICs were observed in the trip blanks. Those compounds are all relatively polar and were associated with difficult to remove contamination of the sample preparation stainless steel manifold. The problem was eventually corrected but could not be completely eliminated within the time frame of the field sampling schedule. A number of additional compounds were detected in at least one of the blanks at trace levels (below EQL). The other target compounds observed are generally ascribable to contamination during sampling and subsequent handling associated with the use of 3M adhesive tape. Numerous TICs typical of adhesive tape emanations or other background environmental sources (alkanes, alkenes, and cycloalkanes) were also observed including methyl cyclohexane which provides a characteristic signature for the 3M tape. Other compounds which appeared in both field blanks as well as the tank samples were acetaldehyde, 2-propanol, 2-methyl-2-propanol, isopropanol, and 1-fluoro-1.1-dichloroethane. The origin of these compounds is unclear.

Batch 7/19/96:

Samples included in this batch consisted of the three tank samples and one repeat analysis of a tank sample.

The CCV was within nominal limits for all compounds except tetrahydrofuran (29%), carbon tetrachloride (28%), decane (31%), and tetradecane (32%). Internal standard (IS) responses were acceptable for the first five runs but the last sample run had an unusually high IS response. Variations in IS response with this method are associated with minor differences in tube packing density, which can result in a decrease in split ratio and an increased sensitivity. This is true in this case for the last sample run, which showed a higher than normal sensitivity as compared to typical responses that were obtained, for example, during the earlier performance evaluation studies used to estimate quantification limits. The increased sensitivity does not negatively impact data quality. Results are similar to those obtained on the other three runs. Rerun of the sample was not possible.

The samples contained numerous target compounds at levels in excess of the EQL including methanol, butane, ethanol, acetonitrile, acetone, trichlorofluoromethane, pentane, propanol, propanenitrile, 2-butanone, hexane, tetrahydrofuran, butanenitrile, benzene, 1-butanol, cyclohexane, heptane, 4-methyl-2-pentanone, pentanenitrile, toluene, ethylbenzene, p/m xylene, styrene, o-xylene, nonane, and decane. Compounds also seen in field blanks at levels in excess of the EQL included acetone, propanol, propanenitrile, 2-butanone, hexane, tetrahydrofuran, butanenitrile, 1-butanol, cyclohexane, heptane, 4-methyl-2-pentanone, pentanenitrile, toluene, ethylbenzene, p/m xylene, styrene, o-xylene, and decane. Compounds also observed in the trip blanks at levels in excess of the EQL included propanol, propanenitrile, 2-butanone, tetrahydrofuran, butanenitrile, and 4-methyl-2-pentanone. Data associated with those compounds should be flagged as suspect. A number of other target compounds were detected in at least one of the samples at trace levels (below EQL). Many of the target compounds observed (bolded) are generally ascribable to contamination during sampling and subsequent handling associated with the use of 3M adhesive tape. Methanol was also present in the field blanks at trace levels, which probably represent a passive

sampling contribution of about 10% since that compound is not typically associated with adhesive tape or other probable environmental sources. Numerous TICs typical of adhesive tape emanations were also observed including methyl cyclohexane, which provides a characteristic signature for the 3M tape. Other compounds that showed up in the tank samples were acetaldehyde, 2-propanol, 2-methyl-2-propanol, isopropanol and 1-fluoro-1,1-dichloroethane. These compounds were also present in the field blanks but at much lower levels, perhaps representing passive sampling.

Sample volumes for all ISVS samples have been corrected to STP from the 21°C calibration used on the sampling cart flowmeters. The correction was included in the reported data to provide seamless compatibility with past VSS data that were collected using a 0°C calibration.

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank U-112 on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time (mg/m ³)	S6071-A11.1090 ^(c) ISVS		S6071-A12.1091 ^(c) ISVS		S6071-A13.1092 ^(c) ISVS		Mean and Standard Deviation						
				(ppbv)	Flag	(ng/m ³)	Flag	(ng/m ³)	Flag	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.			
Methanol	67-56-1	32	10.0	1.354	946	Y	1.028	719	Y	0.867	606	Y	1.083	0.248	757	173
Butane	106-97-8	58	10.8	0.084	32		0.059	23		0.060	23		0.068	0.014	26	5.5
Ethanol	64-17-5	46	12.6	0.473	230	Y	0.275	134	Y	0.355	173	Y	0.368	0.100	179	48
Acetonitrile	75-05-8	41	13.1	0.056	31		0.046	25		0.047	26		0.050	0.005	27	3.0
Acetone	67-64-1	58	13.7	0.195	75		0.204	79		0.161	62		0.187	0.023	72	8.7
Trichlorofluoromethane	75-69-4	137	14.2	0.532	87		0.525	86		0.528	86		0.529	0.004	86	0.58
Pentane	109-66-0	72	15.0	0.036	11		0.033	10		0.023	7.0	J	0.031	0.007	9.5	2.2
Methylene Chloride	75-09-2	85	15.8	0.119	31	J	0.060	16	J	0.100	26	J	0.093	0.030	24	7.9
1,1,1-Trichloroethane	76-13-1	187	16.3	0.012	1.4	J	0.004	0.50	J	0.003	0.32	J	0.006	0.005	0.73	0.57
Propanenitrile	107-12-0	55	17.1	0.054	22		0.045	18		0.047	19		0.048	0.005	20	1.9
Propanol	71-23-8	60	17.1	0.133	50		0.104	39		0.105	39		0.114	0.017	43	6.2
2-Butanone	78-93-3	72	18.6	0.060	19		0.057	18		0.065	20		0.060	0.004	19	1.3
Hexane	110-54-3	86	19.9	0.048	12		0.047	12		0.038	9.8		0.044	0.006	12	1.5
Tetrahydrofuran	109-99-9	72	20.8	0.139	43		0.132	41		0.142	44		0.138	0.005	43	1.5
Butanenitrile	109-74-0	69	21.9	0.058	19		0.050	16		0.051	17		0.053	0.004	17	1.4
Benzene	71-43-2	78	22.8	0.017	4.9		0.016	4.7		0.018	5.1		0.017	0.001	4.9	0.22
1,1,1-Trichloroethane	71-55-6	133	22.0	0.024	4.0	J	0.023	3.9	J	0.024	4.1	J	0.024	0.001	4.0	0.090
1-Butanol	71-36-3	74	22.3	0.280	85		0.254	77		0.299	90		0.277	0.023	84	6.9
Carbon Tetrachloride	56-23-5	154	23.1	0.006	0.86	J	0.007	0.94	J	0.008	1.1	J	0.007	0.001	0.96	0.12
Cyclohexane	110-82-7	84	23.4	0.109	29		0.106	28		0.063	17		0.093	0.026	25	6.9
Trichloroethene	79-01-6	131	24.8	0.004	0.74	J	0.004	0.63	J	0.004	0.73	J	0.004	0.000	0.70	0.061
Heptane	142-82-5	100	25.2	0.302	67		0.294	66		0.210	47		0.268	0.051	60	11
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.068	15		0.059	13		0.052	12		0.060	0.008	13	1.8
Pyridine	110-86-1	79	26.6	0.088	25	J	0.079	22	J	0.084	24	J	0.084	0.004	24	1.3
Pentanenitrile	110-59-8	83	27.4	0.010	2.7		0.009	2.4		0.009	2.5		0.009	0.001	2.5	0.15
Toluene	108-88-3	92	28.5	1.055	256		1.081	263		0.827	201		0.988	0.139	240	34
Octane	111-65-9	114	30.5	0.013	2.5	J	0.017	3.3	J	0.013	2.6	J	0.014	0.002	2.8	0.44
Tetrachloroethylene	127-18-4	166	31.1	0.014	1.9	J	0.012	1.6	J	0.017	2.2	J	0.014	0.003	1.9	0.34
Hexanenitrile	628-73-9	97	32.8	0.006	1.4	J	0.006	1.4	J	0.003	0.78	J	0.005	0.001	1.2	0.34
Ethylbenzene	100-41-4	106	33.5	0.077	16		0.095	20		0.062	13		0.078	0.016	16	3.4
p/m-Xylene	106-42-3	106	33.9	0.273	58		0.317	67		0.209	44		0.266	0.054	56	11
Styrene	100-42-5	104	34.8	0.052	11		0.062	13		0.042	8.9		0.052	0.010	11	2.2
o-Xylene	95-47-6	106	35.1	0.104	22		0.117	25		0.078	16		0.100	0.020	21	4.2
Nonane	111-84-2	128	35.5	0.019	3.3		0.021	3.6		0.014	2.5		0.018	0.003	3.1	0.58
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.006	1.1	J	0.006	1.2	J	0.005	0.87	J	0.006	0.001	1.1	0.17
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.005	0.96	J	0.006	1.1	J	0.005	0.86	J	0.005	0.001	0.96	0.10
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.015	2.7	J	0.016	2.9	J	0.013	2.4	J	0.014	0.001	2.7	0.27
Decane	124-18-5	142	40.2	0.058	9.2		0.057	8.9		0.038	5.9		0.051	0.012	8.0	1.8
1,3-Dichlorobenzene	541-73-1	147	40.5	0.010	1.6	J	0.011	1.6	J	0.008	1.2	J	0.010	0.001	1.5	0.22
1,4-Dichlorobenzene	106-46-7	147	40.7	0.010	1.5	J	0.011	1.6	J	0.008	1.2	J	0.010	0.001	1.5	0.22
Undecane	1120-21-4	156	44.5	0.019	2.7	J	0.019	2.7	J	0.017	2.4	J	0.018	0.001	2.6	0.21

Table E.2. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) for Triple Sorbent Traps Collected from the Headspace of Tank U-112 on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A11.1090 ^(c) ISVS		S6071-A12.1091 ^(c) ISVS		S6071-A13.1092 ^(c) ISVS		Mean and Standard Deviation						
				(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	(ppbv)	(mg/m ³)	St. Dev.	(ppbv)	St. Dev.			
Dodecane	112-40-3	170	48.5	0.009	1.2	J	0.009	1.1	J	0.011	1.5	J	0.010	0.001	1.3	0.19
Tridecane	629-50-5	184	52.3	0.030	3.7	J	0.025	3.1	J	0.019	2.3	J	0.025	0.006	3.0	0.68
Tetradecane	629-59-4	198	55.8	0.030	3.4	J	0.028	3.2	J	0.026	2.9	J	0.028	0.002	3.1	0.23
Tentatively Identified Compounds^(b)																
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	1.593	357	N	0.909	204	N	0.583	131	N	1.028	0.515	230	115
Acetaldehyde	75-07-0	44	9.5	0.219	111	N	0.162	83	N	0.124	63	N	0.169	0.048	86	24
1-Propene, 2-methyl-	115-11-7	56	10.4	0.212	85	N	0.253	101	N	0.149	59	N	0.204	0.052	82	21
Isopropyl Alcohol	67-63-0	60	14.3	0.138	51	N	0.118	44	N	0.127	47	N	0.128	0.010	48	3.6
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.180	35	J	0.230	44	N	0.113	22	N	0.174	0.059	34	11
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.295	89	N	0.315	95	N	0.216	65	N	0.275	0.052	83	16
Hexane, 2-methyl-	591-76-4	100	23.5	0.281	63	N	0.262	59	N	0.196	44	N	0.246	0.045	55	10
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.152	34	N	0.144	32	N	0.122	27	N	0.140	0.016	31	3.5
Hexane, 3-methyl-	589-34-4	100	24.0	0.449	100	N	0.424	95	N	0.338	76	N	0.404	0.058	90	13
Unknown C8 Alkane	114	24.8	0.474	0.474	93	N	0.480	94	N	0.409	80	N	0.455	0.039	89	8
Cyclohexane, methyl-	108-87-2	98	26.7	0.519	119	N	0.474	108	N	0.399	91	N	0.464	0.060	106	14
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.168	33	N	0.180	35	N	0.128	25	N	0.158	0.027	31	5.4
Cyclohexane, 1,4-dimethyl-	589-90-2	112	29.7	0.107	21	N	0.129	26	N	0.083	17	N	0.106	0.023	21	4.6
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.2	1.033	104	N	1.321	133	N	0.993	100	N	1.116	0.179	113	18
Hexane, 2,3,5-trimethyl-	1069-53-0	128	31.5	0.314	55	N	0.389	68	N	0.234	41	N	0.312	0.078	55	14
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	1.358	238	N	1.672	293	N	0.983	172	N	1.338	0.345	234	60
Unknown C9 Alkene/Cycloalkane	126	32.7	0.118	0.118	21	N	0.221	39	N	0.134	24	N	0.157	0.055	28	10
Unknown C9 Alkane	128	33.8	0.238	0.238	42	N	0.330	57	N	nd	nd		0.284	e	50	e
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.5	0.546	41	N	0.685	52	N	0.493	37	N	0.575	0.099	43	7.5
Unknown C12 Alkane	170	42.9	0.970	0.970	128	N	nd	nd		0.683	90	N	0.826	e	109	e

Data Quality Flags
 J Flag denotes target compound detected above Instrument Detection Limit (IDL), but below estimated Quantitation Limit (EQL)
 N Flag denotes tentatively identified compound
 U Flag denotes compound not detected above listed IDL

Footnotes

- (a) Detected target analytes.
 - (b) Semi-quantitative estimate calculated using concentration of closest eluting IS.
 - (c) WHC sample identification number.
 - (d) Replicates of this sample are found in Table D.3.
 - (e) Mean and/or standard deviation are not meaningful for this analyte.
- nd Not detected

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank U-112 on 7/9/96

Target Analytes ^(a)	CAS	MW	Ret Time	S6071-A12.1091 ISVS						Relative Percent Difference ^(d)
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	%
Methanol	67-56-1	32	10.0	1.028	719	Y	0.920	643	Y	11
Butane	106-97-8	58	10.8	0.059	23		0.061	24		4
Ethanol	64-17-5	46	12.6	0.275	134	Y	<0.275	< 133	Y	
Acetonitrile	75-05-8	41	13.1	0.046	25		0.050	27		8
Acetone	67-64-1	58	13.7	0.204	79		0.191	74		7
Trichlorofluoromethane	75-69-4	137	14.2	0.525	86		0.508	83		3
Pentane	109-66-0	72	15.0	0.033	10		0.032	9.9		3
Methylene Chloride	75-09-2	85	15.8	0.060	16	J	0.080	21	J	28
1,1,2-trichloro-2,2,2-trifluoroethane	76-13-1	187	16.3	0.004	0.50	J	0.005	0.57	J	16
Propanenitrile	107-12-0	55	17.1	0.045	18		0.043	17		4
Propanol	71-23-8	60	17.1	0.104	39		0.080	30		26
2-Butanone	78-93-3	72	18.6	0.057	18		0.053	16		7
Hexane	110-54-3	86	19.9	0.047	12		0.046	12		3
Tetrahydrofuran	109-99-9	72	20.8	0.132	41		0.129	40		3
Butanenitrile	109-74-0	69	21.9	0.050	16		0.048	16		3
Benzene	71-43-2	78	22.8	0.016	4.7		0.017	4.9		4
1,1,1-Trichloroethane	71-55-6	133	22.0	0.023	3.9	J	0.023	3.9	J	1
1-Butanol	71-36-3	74	22.3	0.254	77		0.224	68		13
Carbon Tetrachloride	56-23-5	154	23.1	0.007	0.94	J	0.005	0.78	J	18
Cyclohexane	110-82-7	84	23.4	0.106	28		0.107	29		1
Trichloroethene	79-01-6	131	24.8	0.004	0.63	J	0.004	0.67	J	5
Heptane	142-82-5	100	25.2	0.294	66		0.284	64		3
4-Methyl-2-Pentanone	108-10-1	100	26.4	0.059	13		0.048	11		20
Pyridine	110-86-1	79	26.6	0.079	22	J	0.071	20	J	11
Pentanenitrile	110-59-8	83	27.4	0.009	2.4		0.008	2.2	J	6
Toluene	108-88-3	92	28.5	1.081	263		1.072	261		1
Octane	111-65-9	114	30.5	0.017	3.3	J	0.016	3.2	J	2
Tetrachloroethylene	127-18-4	166	31.1	0.012	1.6	J	0.014	1.8	J	15
Hexanenitrile	628-73-9	97	32.8	0.006	1.4	J	0.005	1.1	J	26
Ethylbenzene	100-41-4	106	33.5	0.095	20		0.093	20		1
p/m-Xylene	106-42-3	106	33.9	0.317	67		0.320	67		1
Styrene	100-42-5	104	34.8	0.062	13		0.060	13		2
o-Xylene	95-47-6	106	35.1	0.117	25		0.116	24		1
Nonane	111-84-2	128	35.5	0.021	3.6		0.020	3.6		1
1-Ethyl-2-methyl benzene	611-14-3	120	38.5	0.006	1.2	J	0.012	2.2	J	61
1,3,5-Trimethylbenzene	108-67-8	120	38.7	0.006	1.1	J	0.006	1.1	J	5
1,2,4-Trimethylbenzene	95-63-6	120	40.0	0.016	2.9	J	0.015	2.9	J	3
Decane	124-18-5	142	40.2	0.057	8.9		0.054	8.6		5
1,3-Dichlorobenzene	541-73-1	147	40.5	0.011	1.6	J	0.011	1.7	J	2
1,4-Dichlorobenzene	106-46-7	147	40.7	0.011	1.6	J	0.011	1.7	J	2
Undecane	1120-21-4	156	44.5	0.019	2.7	J	0.020	2.8	J	5
Dodecane	112-40-3	170	48.5	0.009	1.1	J	0.009	1.2	J	6
Tridecane	629-50-5	184	52.3	0.025	3.1	J	0.023	2.8	J	10
Tetradecane	629-59-4	198	55.8	0.028	3.2	J	0.023	2.6	J	18
Tentatively Identified Compounds^(b)										
Ethane, 1-chloro-1,1-difluoro-	75-68-3	100	8.8	0.909	204	N	0.747	167	N	20
Acetaldehyde	75-07-0	44	9.5	0.162	83	N	0.060	31	N	92
1-Propene, 2-methyl-	115-11-7	56	10.4	0.253	101	N	0.238	95	N	6
Isopropyl Alcohol	67-63-0	60	14.3	0.118	44	N	0.119	45	N	1
1-Fluoro-1,1-dichloro-ethane	0-00-0	116	14.4	0.230	44	N	0.216	42	N	6
2-Propanol, 2-methyl-	75-65-0	74	15.5	0.315	95	N	0.294	89	N	7

Table E.3. Positively Identified and Quantitated Target Analytes^(a) and Tentatively Identified Compounds and Estimated Concentrations^(b) of Replicate Analysis of a Single Triple Sorbent Trap Collected from the Headspace of Tank U-112 on 7/9/96

Tentatively Identified Compounds ^(b)	CAS	MW	Ret Time	S6071-A12.1091 ISVS						Relative Percent Difference ^(d) %
				(mg/m ³)	(ppbv)	Flag	(mg/m ³)	(ppbv)	Flag	
Pentane, 3,3-dimethyl-	562-49-2	100	23.0	nd	nd		0.045	10	N	
Hexane, 2-methyl-	591-76-4	100	23.5	0.262	59	N	0.242	54	N	8
Pentane, 2,3-dimethyl-	565-59-3	100	23.7	0.144	32	N	0.141	32	N	2
Hexane, 3-methyl-	589-34-4	100	24.0	0.424	95	N	0.404	91	N	5
Unknown C8 Alkane		114	24.8	0.480	94	N	0.457	90	N	5
Cyclohexane, methyl-	108-87-2	98	26.7	0.474	108	N	0.464	106	N	2
Hexane, 2,4-dimethyl-	589-43-5	114	27.1	0.180	35	N	0.172	34	N	5
Cyclohexane, 1,4-dimethyl-	589-90-2	112	29.7	0.129	26	N	0.129	26	N	0
Cyclotrisiloxane, hexamethyl-	541-05-9	222	31.2	1.321	133	N	1.348	136	N	2
Hexane, 2,3,5-trimethyl-	1069-53-0	128	31.5	0.389	68	N	0.381	67	N	2
Heptane, 2,4-dimethyl-	2213-23-2	128	31.8	1.672	293	N	1.641	287	N	2
Unknown C9 Alkene/Cycloalkane		126	32.7	0.221	39	N	0.221	39	N	0
Unknown C9 Alkane		128	33.8	0.330	57	N	0.303	53	N	9
Cyclotetrasiloxane, octamethyl-	556-67-2	296	39.5	0.685	52	N	0.680	51	N	1
Unknown C12 Alkane		170	42.9	nd	nd		0.973	128	N	

Data Quality Flags

J Target compound detected above the IDL but below the EQL.

N Denotes tentatively identified compound

U Target compound not detected at or above the IDL.

Y Initial calibration and CCV was performed; however, the analyte was not part of the current operating procedure.

Footnotes

(a) Detected target analytes.

(b) Semi-quantitative estimate calculated using concentration of closest eluting IS.

(c) WHC sample identification number.

(d) Relative percent differences (RPDs) based on mg/m³ values.

nd Not detected

Appendix F

Tank Vapor Characterization: Chain of Custody Sample Control Forms

Custody Form Initiator J. A. Edwards - PNNL Telephone (509) 373-0141
Page 85-3009 / FAX 376-2329

Company Contact R. D. Mahon - WHC Telephone (509) 373-7437
Page 85-9656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm Collection date 07 - 09 - 96
241-U-112 Tank Vapor Sample SAF S6071 Preparation date 07 - 08 - 96
(ISVS Cart)

Ice Chest No. Field Logbook No. WHC- N-647-8

Bill of Lading/Airbill No. N/A Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6071 - A07 . 28R Collect NH₃/NO_x/H₂O Sorbent Trap
S6071 - A08 . 29R Collect NH₃/NO_x/H₂O Sorbent Trap
S6071 - A09 . 30R Collect NH₃/NO_x/H₂O Sorbent Trap
S6071 - A10 . 31R Collect NH₃/NO_x/H₂O Sorbent Trap

S6071 - A15 . 32R Open, close and store NH₃/NO_x/H₂O field blank #1
S6071 - A16 . 33R Open, close and store NH₃/NO_x/H₂O field blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
G W Dennis <i>H.W.D.</i>	07-08-96	1335	J A Edwards <i>J A Edwards</i>	07-08-96	1335
J A Edwards <i>J A Edwards</i>	07-08-96	1445	ES MAST <i>ES MAST</i>	07-08-96	1445
ES MAST <i>ES MAST</i>	7-16-96	1545	J A Edwards <i>J A Edwards</i>	7-16-96	1545
J A Edwards <i>J A Edwards</i>	7-17-96	1320	G.W. Dennis <i>H.W.D.</i>	7-17-96	1320
G.W. Dennis <i>H.W.D.</i>	7-18-96	1230	K.H. Pool <i>Karl Pool</i>	7-18-96	1230

Final Sample Disposition

Comments:

RETURNED WITH 'RAD' TAGS & YELLOW BAGGED - Kim Barton (RCF) SURVEY @ 07/16/96

- | PNNL (only) Checklist | Pick-up / Delivery | Comments: |
|------------------------------------|--------------------|-----------|
| Media labeled and checked? | Y/N | |
| Letter of instruction? | Y/N | |
| Media in good condition? | Y/N / Y/N | |
| COC info/signatures complete? | Y/N / Y/N | |
| Rad release stickers on samples? | Y/N / Y/N | |
| Activity report from 222S? | Y/N / Y/N | |
| RSR/release? (a ≤100/B ≤400 pCi/g) | Y/N / Y/N | |
| COC copy for LRB, RIDS filed? | Y/N / Y/N | |

Battelle Pacific
National Northwest Lab

CHAIN OF CUSTODY

WHC 100250

Custody Form Initiator J. A. Edwards - PNNL Telephone (509) 373-0141
Page 85-3009 / FAX 376-2329

Company Contact R. D. Mahon - WHC Telephone (509) 373-2891
Page 85-3656 / FAX 373-3793

Project Designation/Sampling Locations 200 West Tank Farm Collection date 07 - 09 - 96
241-U-112 Tank Vapor Sample SAF S6071 Preparation date 07 - 08 - 96
(ISVS Cart)

Ice Chest No. Field Logbook No. WHC-N-647-8

Bill of Lading/Airbill No. N/A Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to PNNL

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6071 - A01 . 091 Collect Ambient Air Sample SUMMA #1
S6071 - A02 . 092 Collect Ambient Air Sample SUMMA #2 (through tube bundle)

S6071 - A04 . 093 Collect SUMMA #3
S6071 - A05 . 183 Collect SUMMA #4
S6071 - A06 . 333 Collect SUMMA #5

<input type="checkbox"/> Field Transfer of Custody		<input checked="" type="checkbox"/> Chain of Possession		(Sign and Print Names)		
Relinquished By	Date	Time	Received By	Date	Time	
J A Edwards <i>J A Edwards</i>	07-08-96	1445	ES MAST <i>ES MAST</i>	07-08-96	1445	
ES MAST <i>ES MAST</i>	7-16-96	1545	J A EDWARDS <i>J A EDWARDS</i>	7-16-96	1545	

Final Sample Disposition

Comments:

PNNL (only) Checklist Pick-up / Delivery Comments:

Media labeled and checked? Y N

Letter of instruction? Y N

Media in good condition? Y N / Y N

COC info/signatures complete? Y N / Y N

Rad release stickers on samples? Y N / Y N

Activity report from 222S? Y N / Y N

RSR/release? (a ≤100/B ≤400 pCi/g) Y N / Y N

COC copy for LRB, RIDS filed? Y N / Y N

POC POC

(WHC-SD-WM-TP-335, REV. 2, Table 2b)

(Revised 05/30/96 PNNL)

Custody Form Initiator J. A. Edwards - PNL

Telephone (509) 373-0141
Page 85-3009 / P8-08 / FAX 376-0418

Company Contact R. D. Mahon - WHC

Telephone (509) 373-7437
Page 85-9656 / S3-27 / FAX 373-7076

Project Designation/Sampling Locations 200 West Tank Farm
241-U-112 Tank Vapor Sample SAF S6071
(ISVS Cart)

Collection date 07 - 07 - 96
Preparation date 07 - 07 - 96

Ice Chest No.

Field Logbook No. WHC-N-6978

Ertco Hi/Lo thermometer No. PNL-T-006

Bill of Lading/Airbill No. N/A

Offsite Property No. N/A

Method of Shipment Government Truck

Shipped to WHC

Possible Sample Hazards/Remarks Unknown at time of sampling

Sample Identification

S6071 - A11 . 1090 PNL Triple Sorbent Trap (TST) Sample # 1
S6071 - A12 . 1091 PNL TST Sample # 2
S6071 - A13 . 1092 PNL TST Sample # 3
S6071 - A14 . 1093 PNL TST Sample # 4

S6071 - A17 . 1094 Open, close & store TST Field Blank # 1
S6071 - A18 . 1095 Open, close & store TST Field Blank #2

S6071 - A19 . 1096 Store TST Trip Blank #1
S6071 - A20 . 1097 Store TST Trip Blank #2

[] Field Transfer of Custody		[X] Chain of Possession		(Sign and Print Names)	
Relinquished By	Date	Time	Received By	Date	Time
JL Julia <i>(Signature)</i>	07-08-96	9:30A	JA Edwards <i>(Signature)</i>	07-08-96	0730
JA Edwards <i>(Signature)</i>	07-08-96	1445	ESMIST S. M...	07-08-96	1445
ESMIST S. M...	7-16-96	1545	JA Edwards	07-16-96	1545
JA Edwards <i>(Signature)</i>	07-17-96	0950	JL Julia <i>(Signature)</i>	07-17-96	0950

Final Sample Disposition

Comments:

PNL (only) Checklist

- Media labeled and checked? Y/N
- Letter of instruction? Y/N
- Media in good condition? Y/N
- COC info/signatures complete? Y/N
- Sorbents shipped on ice? (<5°C) Y/N
- Hi/Lo thermometer - Keep upright! Y/N
- Hi/Lo thermometer Y/N
- Rad release stickers on samples? Y/N
- Activity report from 222S? Y/N
- COC copy for LRB, RIDS filed? Y/N

POC *(Signature)* POC *(Signature)*

Comments:

RETURNED WITH 'RAD' TAGS & YELLOW BAGGED
- Kim Barton (RCF) SURVEY 07/16/96

Cooler Temperature Status

Hi -20°C / Lo -20°C (pick up at PNL to WHC)
Hi +2°C / Lo +2°C (delivery at WHC from PNL)
Hi _____°C / Lo _____°C (at return to PNL from WHC)
Hi +7°C / Lo _____°C (at delivery from WHC to PNL)

(Revised 06/21/95 PNL)

Distribution List

PNNL-11265

PNNL

Karl Pool	P8-08
Berta Thomas	P8-08
John Evans	K6-96
Khris Olsen	K6-96
Kurt Silvers	K9-08
Jon Fruchter	K6-96
Jim Huckaby	K6-80
Brenda Thornton	K6-80
Darlene Varley	K1-06
Katherine Savard	K9-04
Kris Walters	K6-80 (5 copies)

Lockheed

Larry Pennington	S7-21
Luther Buckley	R2-12

DOE-RL

Carol Babel	S7-54
Jim Thompson	S7-54